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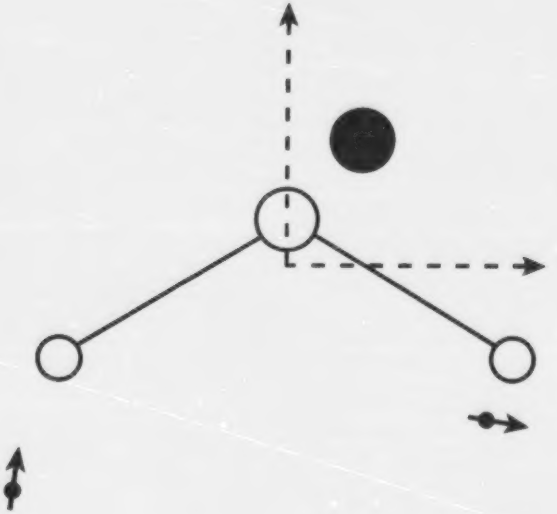

Philip R. Bunker
and Per Jensen

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Molecular Symmetry and Spectroscopy

Second edition

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Molecular Symmetry and Spectroscopy

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Second edition

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This book is dedicated to Gerhard Herzberg

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From Preface to Edition 1

This is a book about the use of group theory in quantum mechanics with particular reference to problems in molecular spectroscopy. There are so many books, so many good books, on this subject that it is hard to believe that there can be any justification for writing another. The justification lies in the fact that whereas the existing literature is concerned with the use of the molecular point group, whose elements consist of rotation and reflections of vibronic variables, the present volume discusses the use of the molecular symmetry group, whose elements consist of permutations of identical nuclei with or without the inversion. The molecular symmetry group is of more general use than the molecular point group since the effect of molecular rotation and the effect of tunneling due to nonrigidity (such as inversion tunneling in the ammonia molecule) are allowed for. Also, because of the fundamental nature of its elements, the molecular symmetry group provides a very good pedagogical vehicle for teaching group theory and the application of group theory to problems in molecular spectroscopy.

The book is aimed at the serious student of molecular spectroscopy, and although knowledge of the postulatory basis of quantum mechanics is assumed, group theory is developed from first principles. I hope that the reader will gain from this book a good understanding of the place of the molecular symmetry group, in relation to the molecular point group and the molecular rotation group, in the application of group theory to problems in molecular spectroscopy. To aid in this understanding I have included many applications of the ideas as they arise and many figures to show the effect of symmetry operations. I have also included problems, followed by worked solutions, in the body of the text; as a result of this the reader can "self pace" his reading by either (a) omitting to read the problems and solutions, (b) solving the problems as they arise (and then reading the solution in the text as a check), or (c) reading the problems and solutions and treating them as a continuing part of the text.

Acknowledgments for Edition 1

I am very grateful to D.M. Bishop, J. M. Brown, R. E. Moss, T. Nakagawa, and M. Vernon who each read the entire book in manuscript form and gave much helpful advice in order to improve it. I an also grateful to H. H. Günthard, J. Hardwick, G. Hills, J. T. Hougen, V. Laurie, I. M. Mills, A. R. W. McKellar, M. T. Riggin, and S. Novick for their advice on particular points. M. Herman, J. K. G. Watson, and B. P. Winnewisser each read and corrected the proofs of the book, and my wife Éva, together with M. B. Wadworth and A. M. Lyyra, helped me to compare the proofs with the typewritten manuscript; I am very grateful for their help.

I would especially like to thank Helen Letaif who typed the entire final draft of the manuscript and a special effort to ensure a well produced and consistent product. Assisting in the typing of the first draft and in typing the modifications that I made to the second draft were Denise Charette, Gloria Dumoulin, Marilyn Nadon, and Lorette Ernst; I very much appreciate all their help.

Ottawa, Canada
January 1978

P. R. BUNKER

Preface to Edition 2

In this edition we have reorganized the material that was in Edition 1 and have significantly enlarged the treatment. We have reorganized the material so that the molecular symmetry (MS) group is introduced much earlier on (in Chapter 3 rather than in Chapter 9). We have also consolidated the explanation of how to determine nuclear spin statistics in Chapter 8 since this is a useful and simple application of the MS group. Previously this material was scattered throughout several chapters. Enlargements have resulted for several reasons. We consider in more depth the symmetry of molecular states in the three-dimensional rotation group $\boldsymbol{K}$(spatial), and along with this we discuss angular momentum theory, the use of irreducible spherical tensor operators, the Wigner-Eckart theorem and vector coupling coefficients. We follow the conventions and notation of the book by Zare (1988), and one should refer to Zare's book for a more detailed discussion of these aspects of molecular symmetry. Enormous progress has been made in both the theoretical and experimental study of weakly bound cluster molecules (often called van der Waals molecules) and we include a detailed treatment of these systems (in Chapters 3 and 16); the use of the MS group is vital for them. It also turns out that the irreducible spherical tensor operator technique is perfectly adapted for expanding the potential function and dipole moment of such molecules, and this allows us to appreciate the form of appropriate basis functions and to determine optical selection rules. Since we aim to teach by example we discuss the hydrogen dimer and the ammonia dimer in detail. There has been much progress in the study of the spectra of rigid molecules and nonrigid molecules (apart from weakly bound cluster molecules) since 1979 and this has resulted in the inclusion of additional material. The discussion of Energy Levels and Interactions (in Chapter 13), and of Transition Intensities and Optical Selection Rules (in Chapter 14) contains a great deal of material that was not in Edition 1, such as that on the Jahn-Teller effect, the Renner effect, Multichannel Quantum Defect Theory, and the use of variational methods for calculating rotation-vibration energy levels. In Chapter 13 we also give an account of the theory of the contact transformed rotation-vibration Hamiltonian which is discussed at more length in the book by Papoušek and Aliev (1982) and in the review by Aliev and Watson (1985). In the treatment of examples of nonrigid molecules given in Chapter 15 we explain the understanding achieved of the fundamentally important molecules ethane, dimethylacetylene, nitromethane, hydrogen peroxide, toluene, and ethylene; for all of these molecules the MS group adds enormously to our understanding. We include a selection of experimental spectra to illustrate particular theoretical points.

One normally only reads a newspaper if its political leanings are in the same direction as one's own. A similar choice is made before reading a scientific textbook, particularly one involving group theory. Therefore, it beholds us to tell you what our prejudices are. We are first and foremost interested in ***understanding*** molecules, and their interaction with electromagnetic radiation, as revealed by the study of high resolution (normally rotationally resolved) spectroscopy. We are particularly interested in the way that group theory (really representation theory) helps in this understanding. The algebraic intricacies of group theory concern us only to the extent that they produce results of use in molecular physics. For similar reasons we do not discuss in any detail vast brute-force machine calculations of energy levels using basis sets chosen for mathematical convenience rather than physical relevance, but we do recognize the usefulness of such calculations for producing, at least for very small molecules, highly accurate predictions of spectra, and for serving as benchmarks against which the results of more approximate calculations can be tested. This book, then, is for the high resolution molecular spectroscopist who would like to learn how to understand molecules, and molecular spectra, using group theory. We believe we explain everything one needs to know about group theory in order to achieve this goal. More about the formal theory of groups is given in, for example, Wigner (1959) and Tinkham (1964). We further believe that the best way to learn is by studying examples (although this necessarily takes longer than simply quoting the 'rules') and we choose examples that we feel are the most useful for the high resolution spectroscopist. These examples are not chosen in order to demonstrate the stunning capabilities of the mighty machinery of group theory (although we do show how group theory can efficiently enable one to determine the nuclear spin statistical weights of the highly symmetrical molecule $^{13}C_{60}$). We hope you wish to read on.

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We are very grateful to very many colleagues for advice, encouragement and for the provision of spectra and ideas. It would be impossible to list all the help we received in this way but we are happy to list the names of all who have helped us: Zlatko Bačić, James Brault, Robert Buenker, Bonnie Bullock, Hans Bürger, Claude Cantin, Gordon Drake, Allan East, Wolfgang Ernst, Alberto Gambi, Nicholas Handy, Flemming Hegelund, Gerhard Hirsch, Jon Hougen, John Johns, Alan Kelm, Igor Kozin, Ronald Lees, Robert LeRoy, Holger Lichau, Michael Lock, Robert McKellar, Georg Mellau, Terry Miller, Ian Mills, Richard Moss, Josef Paldus, David Perry, Josef Plíva, Douglas Ritchie, Stephen Ross, Trevor Sears, Isaiah Shavitt, Pavel Soldán, Vladimír Špirko, Wolfgang Stahl, Anthony Stone, Jonathan Tennyson, Vladimir Tyuterev, Ad van der Avoird, James Watson, Brenda, Gisbert and Manfred Winnewisser, and Li-Hong Xu. We have used two figures from Callomon, Dunn and Mills (1966), and we thank the Royal Society of London, and the authors of the article, for permission. PRB is grateful for an Alexander von Humboldt Award that allowed him to spend time at the University of Wuppertal during which part of this book was written. PJ has worked on the book while he was a visiting scientist at the Max Planck Institute of Astrophysics, Garching near Munich, and he is grateful to the MPI, and particularly to Wolfgang Kraemer, for hospitality. Also he has worked on the book while he was an IBERDROLA visiting professor at Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas, Madrid, and he is grateful for hospitality and financial support, in particular to Rafael Escribano and Victor Herrero.

Ottawa, Canada P. R. BUNKER
July 1998

Wuppertal, Germany PER JENSEN
July 1998

Introduction

A molecule possesses structural symmetry that is of the same type as that of a macroscopic body, and it can be described in terms of rotation axes and reflection planes. For example, in its equilibrium configuration a methane molecule and a macroscopic tetrahedron both have the same structural symmetry. This symmetry is specified by saying that the molecule belongs to a certain ***point group***, and the group consists of a definite set of rotation and reflection operations (or elements); for the methane molecule the point group is called $\boldsymbol{T}_{\mathrm{d}}$. In molecular physics great use is made of symmetry. However, in this book the concept of symmetry is based entirely on the invariance group of the molecular Hamiltonian and not on the geometrical symmetry of its equilibrium structure; this leads to the introduction of the molecular symmetry (MS) group and three-dimensional rotation group $\boldsymbol{K}$(spatial). The use of these two groups in helping us to understand molecules and their spectra is what the book is all about, but we do show how point group symmetry comes in, how it is used, and how the two types of symmetry are related.

The treatment given here concerning the symmetry classification of the states of polyatomic molecules in the MS group in comparison to that in the point group can be understood by reference to the symmetry classification scheme used for the states of diatomic molecules. For a homonuclear diatomic molecule such as H_2 the vibronic (vibration–electronic) states are classified or labeled using the molecular point group $\boldsymbol{D}_{\infty h}$. On the other hand the rovibronic (rotation–vibration–electronic) energy levels (sometimes called rotational levels) are labeled simply as +s, +a, −s, or −a depending on whether the rovibronic wavefunction is invariant (+) or changed in sign (−) by the inversion of the molecular coordinates in the center of mass, and on whether it is invariant (s) or changed in sign (a) by the interchange or permutation of the two identical nuclei. Two such classification schemes are also possible for the states of polyatomic molecules, but although the use of the molecular point group to classify vibronic states is the subject of a vast textbook literature, the use of inversion and nuclear permutation symmetry to classify rovibronic states is but little described. Both classification schemes are useful in understanding and categorizing molecular interactions, and in this book emphasis is given to the use of inversion and nuclear permutation symmetry; these symmetry elements constitute the molecular symmetry group.

The molecular point group, whose elements are rotations and reflections of vibronic variables, is used when studying the vibronic levels of a molecule in a given electronic state that has a unique equilibrium configuration with no observable tunneling between configurations (i.e., a rigid molecule). This group is useful in understanding, for example, the infrared and Raman activity of vibrational fundamentals, the terms that can occur in the molecular potential function, and the atomic orbital functions that can be included in a particular molecular orbital. Although the molecular point group is introduced and defined in Chapter 4 here, the reader is referred to the texts listed at the end of the chapter for a more exhaustive discussion.

The molecular symmetry group, whose elements consist of the permutations of identical nuclei with or without inversion, is used when studying rovibronic levels of a molecule and the presence of a unique equilibrium configuration is immaterial. The molecular symmetry group has its origins in the work of Christopher Longuet-Higgins and Jon Hougen. The importance of the molecular symmetry group lies not only in its use for studying nonrigid molecules such as ammonia and the water dimer that have large amplitude internal motions, or for studying electronic transitions in which there are changes in the point group symmetry, but also in the fact that it allows for molecular rotation and can be applied to rovibronic as well as vibronic states.

A simple example of the effect of molecular rotation is provided by the H_3^+ molecule. The H_3^+ molecule has an equilateral triangle equilibrium geometry in its electronic ground state and we use the $\boldsymbol{D}_{3h}$ point group to classify the vibrational states. On the basis of point group symmetry considerations, we would say that this molecule has no electric dipole moment and no allowed electric dipole rotational spectrum. However centrifugal distortion in the rotating molecule can give rise to a nonvanishing electric dipole moment so that the molecule does have a rotational spectrum. The molecular symmetry group of the H_3^+ molecule $\boldsymbol{D}_{3h}(M)$ allows us to understand which rovibration states can interact as a result of centrifugal distortion and to determine which rotational transitions can occur in the spectrum (see Section 14.1.14).

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Diatomic Molecules

Herzberg (1989). Symmetry is discussed on pages 128–140.

Point Groups

Herzberg (1991a). Pages 82–131.

Herzberg (1991b). Pages 563–579.

Tinkham (1964). Chapter 4.

Wilson, Decius, and Cross (1955). See particularly Section 5-5 in which the effect of a point group operation on a molecule is described.

The Molecular Symmetry Group

Longuet-Higgins (1963). The birth of the molecular symmetry group; its general definition is given.

Hougen (1962c). The labor pains before the birth. In this paper the "full molecular point group" for a symmetric top molecule is defined by combining molecular point group operations with overall rotations [see Eqs. (4-5)-(4-6d) here]. It is shown that the elements of the group are permutations of identical nuclei in the molecule with or without inversion. This group is, in fact, the molecular symmetry group of a symmetric top molecule. Longuet-Higgins contribution was to bring nuclear permutations, and the inversion, to the fore as the fundamental elements that define molecular symmetry, and to show which of these elements are useful by introducing the concept of *feasibility* (see Section 3.3).

Hougen (1963). This extends Hougen (1962c) to all nonlinear rigid molecules. This paper also shows how "sense-reversing" symmetry operations (which are called permutation-inversion operations in the molecular symmetry group) transform molecular coordinates. In no case is the right handed molecule fixed axis system inverted to become left handed (see page 497).

Hougen (1964a). The double group of the MS group of dimethylacetylene G_{36}(EM) is defined (see Section 15.4.4). This is the first example of what is now generally called an *extended* MS group.

Watson (1965). It is shown how to determine the reverse correlation table from the irreducible representations of the smaller molecular symmetry group to the irreducible representations of the larger molecular symmetry group (see Section 5.9).

Bunker and Papoušek (1969). This extends the definition of the molecular symmetry group to linear molecules using an extended molecular symmetry group (see Section 17.4.2).

Woodman (1970). The decomposition of a molecular symmetry group using direct and semidirect products is discussed.

Watson (1974). The symmetry condition for a first order Stark effect of a molecular rovibronic level is determined from the molecular symmetry group species of the level and the symmetry species of the space fixed electric dipole moment operator (see Section 14.5).

Bunker (1974). Within the Born-Oppenheimer approximation homopolar isotopically unsymmetric diatomic ions such as HD^+ and $^{14}N^{15}N^+$ have $D_{\infty h}$ point group symmetry and a nonvanishing dipole moment. This paradox is reconciled by considering the transformation properties of the electric dipole moment operator under the effect of the permutation of the nuclei.

Watson (1975). The operations of the MS group and the three-dimensional rotation group are used together to treat the symmetry properties of molecules in electric or magnetic fields (see Sections 14.4 and 14.5).

Bunker (1975). This review paper is devoted to the molecular symmetry group and many nonrigid molecules are discussed.

Hougen (1976). This review paper discusses the coordinates and the symmetry of the methane molecule (see Section 13.2.3).

Dyke (1977). A classification of the rotation-tunneling energy levels of the water dimer in its molecular symmetry group is given. Selection rules and statistical weights are determined.

Bunker (1979a). The spin double groups of molecular symmetry groups are discussed (see Chapter 18).

Hougen (1980). For an ethane molecule in which internal rotation splittings are resolved it is shown that rotation-vibration g-u interactions can occur, and that the extended molecular symmetry group $\boldsymbol{G}_{36}$(EM) can be used to label such interacting states.

Odutola, Alvis, Curtis, and Dyke (1981), and Odutola and Adekola (1987). The character tables of the molecular symmetry groups of weakly bound cluster molecules such as benzene dimer and trimer, and ammonia trimer and tetramer are determined.

Bunker and Howard (1983). The approach used in Edition 1 (and 2) of this book and in Wigner (1959) for generating representation matrices are different, and this paper shows in detail that each is correct and self-consistent. For the MS group, the approach used in this book is (as one might guess) the appropriate one. See the Bibliographical Notes to Chapters 1 and 6 for more details of this point.

Sørensen and Pedersen (1983). Using the molecular symmetry group $\boldsymbol{G}_{12}$ an important rotation-torsion coupling term is shown to be permitted. The characterization of the effect of this perturbation in the microwave spectrum allows the sign of the torsional barrier to be determined (see Section 15.4.2).

Bone, Rowlands, Handy and Stone (1991). It is shown how the transition state for an intramolecular rearrangement can be deduced using the molecular symmetry group. The term *versions* is coined for symmetrically equivalent nuclear equilibrium configurations (see Section 3.2).

Havenith, Linnartz, Zwart, Kips, ter Meulen, and Meerts (1992), Loeser, Schmuttenmaer, Cohen, Elrod, Steyert, Saykally, Bumgarner, and Blake (1992), and van Bladel, van der Avoird, Wormer and Saykally (1992). Experimental and theoretical studies of the ammonia dimer show that the MS group $\boldsymbol{G}_{144}$ is needed to interpret the spectrum (see Section 16.5.2).

Moss (1993). An analysis of electronic g/u interactions in H_2^+ is made using the molecular symmetry group (see Section 17.7).

Jensen and Bunker (1994). A discussion is given of the use of the MS group for making a symmetry analysis of the four-fold rotational energy level clusters that occur for triatomic molecules in high angular momentum states. It leads to an extension of the criteria that one should use to determine whether a permutation-inversion symmetry operation is feasible (see Section 15.4.8).

1

The Complete Nuclear Permutation Group

A permutation operation is defined, and the result of multiplying (or combining) permutations together is explained. The concept of a group is defined, and the complete nuclear permutation (CNP) group of a molecule is introduced. The effect of a nuclear permutation on the nuclear coordinates in a molecule, and on a function of the coordinates, is considered using the methyl fluoride and ethylene molecules as examples.

1.1 THE DEFINITION OF A PERMUTATION OPERATION

Permutations change the order of an ordered set of numbers. For example, the numbers 1, 2, and 3 can be ordered as

$$\underline{123},\ \underline{132},\ \underline{213},\ \underline{231},\ \underline{312},\ \text{or}\ \underline{321}, \tag{1-1}$$

and permutations take us from one ordering to another. The permutation of the numbers 1 and 3 changes the order from $\underline{213}$ to $\underline{231}$, for example, and introducing the notation (13) for the operation of permuting 1 and 3 we write

$$(13)\underline{213} = \underline{231}. \tag{1-2}$$

To change the number order from $\underline{321}$ to $\underline{132}$, the number 1 is replaced by 2, 2 is not replaced by 1 but by 3, and 3 is replaced by 1; we define this as the permutation (123) so that

$$(123)\underline{321} = \underline{132}. \tag{1-3}$$

In the notation used throughout this book $(abcd\cdots yz)$ is a permutation operation that replaces a by b, b by c, c by d, $\ldots$, y by z, and z by a. Other possible permutations of the numbers 1, 2, and 3 are (12), (23), and (132). The permutations (12), (23), and (13) are called ***transpositions*** or ***interchanges***, and (123) and (132) are called ***cycles***. If we permute more than three numbers we can have longer cycles. The following identities hold

$$\begin{aligned} &(12) \equiv (21), \qquad (23) \equiv (32), \qquad (13) \equiv (31), \\ &(123) \equiv (231) \equiv (312), \qquad (132) \equiv (321) \equiv (213). \end{aligned} \tag{1-4}$$

An alternative notation for permutations can be used in which a permutation that replaces 1 by α_1, 2 by α_2, …, n by α_n is denoted

$$\begin{pmatrix} 1 & 2 & \cdots & n \\ \alpha_1 & \alpha_2 & \cdots & \alpha_n \end{pmatrix}. \tag{1-5}$$

A permutation that we would write as $(abcd\cdots yz)$ would be written in the notation of Eq. (1-5) as

$$\begin{pmatrix} a & b & c & \cdots & y & z \\ b & c & d & \cdots & z & a \end{pmatrix}. \tag{1-6}$$

In this notation the order of the columns is immaterial. We can write the five permutations of the numbers 1, 2, and 3 as

$$\begin{gathered} (12) \equiv \begin{pmatrix} 123 \\ 213 \end{pmatrix}, \qquad (23) \equiv \begin{pmatrix} 123 \\ 132 \end{pmatrix}, \qquad (13) \equiv \begin{pmatrix} 123 \\ 321 \end{pmatrix}, \\ (123) \equiv \begin{pmatrix} 123 \\ 231 \end{pmatrix}, \qquad \text{and} \qquad (132) \equiv \begin{pmatrix} 123 \\ 312 \end{pmatrix}. \end{gathered} \tag{1-7}$$

Problem 1-1. Which of the five distinct permutations in Eq. (1-4) changes the number order (a) from $\underline{123}$ to $\underline{132}$, (b) from $\underline{132}$ to $\underline{321}$, and (c) from $\underline{123}$ to $\underline{321}$?

Answer. (a) (23), (b) (132), and (c) (13).

Problem 1-2. If we label the protons in a CH_3F molecule with the numbers 1, 2, and 3 (see Fig. 1-1a on page 8, for example) we find that there are two distinct labeled forms: one with an anticlockwise labeling arrangement (looking along the C → F direction) and one, as in Fig. 1-1a, with a clockwise labeling arrangement. On applying the five distinct permutations of Eq. (1-4) to the labels, what do you notice about the effect of (12), (23), or (13) when compared to the effect of (123) or (132)?

Answer. The permutations (12), (23), and (13) all interconvert the clockwise and anticlockwise labeled forms whereas (123) and (132) preserve the form.

Problem 1-2 is the first example we have met of permuting nuclei in a molecule and it requires further discussion. The permutation (12) is an operation that interchanges the nuclei labeled 1 and 2 and as a result, if the coordinates of nuclei 1 and 2 in a space fixed (X, Y, Z) axis system are initially (X_1, Y_1, Z_1) and (X_2, Y_2, Z_2), respectively, then after applying (12) they become (X_2, Y_2, Z_2) and (X_1, Y_1, Z_1), respectively; the nuclei are interchanged and thereby gain each other's coordinates. We can write

$$(12)[\underbrace{X_1, Y_1, Z_1}_{\textcircled{1}}, \underbrace{X_2, Y_2, Z_2}_{\textcircled{2}}, \ldots] = [\underbrace{X_1, Y_1, Z_1}_{\textcircled{2}}, \underbrace{X_2, Y_2, Z_2}_{\textcircled{1}}, \ldots] \tag{1-8}$$

$$\equiv [\underbrace{X_2, Y_2, Z_2}_{\textcircled{1}}, \underbrace{X_1, Y_1, Z_1}_{\textcircled{2}}, \ldots], \tag{1-9}$$

where the circled numbers represent the nuclei and the braces indicate their coordinates. Equation (1-8) shows the exchange of the nuclei 1 and 2, and Eq. (1-9) is just a reordering so that the coordinates of nucleus 1 are given first. An abbreviated notation in which the nuclear labels (i.e., the numbers in circles) are omitted but in which the coordinates of nucleus 1 are always given first, those of 2 second, etc., can be used so that we have

$$\begin{aligned}(12)[X_1, Y_1, Z_1, X_2, Y_2, Z_2, W] &= [X_1', Y_1', Z_1', X_2', Y_2', Z_2', W'] \\ &\equiv [X_2, Y_2, Z_2, X_1, Y_1, Z_1, W]. \qquad (1\text{-}10)\end{aligned}$$

In Eq. (1-10) (X_i, Y_i, Z_i) are the initial coordinates of nucleus i, W represents the other coordinates in the molecule, and (X_i', Y_i', Z_i') are the coordinates of nucleus i after the permutation has been performed; clearly $W' \equiv W$.

Problem 1-3. Write down equations similar to Eqs. (1-8)-(1-10) for the effect of (123) on the spatial coordinates of the labeled protons in a CH_3F molecule.

Answer. Let us initially give protons 1, 2, and 3 the coordinates (X_1, Y_1, Z_1), (X_2, Y_2, Z_2), (X_3, Y_3, Z_3), respectively, in the space fixed (X, Y, Z) system. The permutation (123) replaces proton 1 by proton 2 so that proton 2 then has as new coordinates the coordinates that proton 1 had initially, i.e., (X_1, Y_1, Z_1). Similarly (123) replaces 2 by 3 so that 3 then has the coordinates that 2 had, i.e., (X_2, Y_2, Z_2), and finally 1 ends up with the coordinates (X_3, Y_3, Z_3) that 3 had. We can write

$$\begin{aligned}&(123)[\underbrace{X_1, Y_1, Z_1}_{\textcircled{1}}, \underbrace{X_2, Y_2, Z_2}_{\textcircled{2}}, \underbrace{X_3, Y_3, Z_3}_{\textcircled{3}}, \ldots] \\ &\quad = [\underbrace{X_1, Y_1, Z_1}_{\textcircled{2}}, \underbrace{X_2, Y_2, Z_2}_{\textcircled{3}}, \underbrace{X_3, Y_3, Z_3}_{\textcircled{1}} \ldots] \qquad (1\text{-}11) \\ &\quad \equiv [\underbrace{X_3, Y_3, Z_3}_{\textcircled{1}}, \underbrace{X_1, Y_1, Z_1}_{\textcircled{2}}, \underbrace{X_2, Y_2, Z_2}_{\textcircled{3}}, \ldots], \qquad (1\text{-}12)\end{aligned}$$

or omitting the circled numbers,

$$\begin{aligned}&(123)[X_1, Y_1, Z_1, X_2, Y_2, Z_2, X_3, Y_3, Z_3, W] \\ &\quad = [X_1', Y_1', Z_1', X_2', Y_2', Z_2', X_3', Y_3', Z_3', W'] \\ &\quad \equiv [X_3, Y_3, Z_3, X_1, Y_1, Z_1, X_2, Y_2, Z_2, W], \qquad (1\text{-}13)\end{aligned}$$

where, here, (X_i', Y_i', Z_i') are the coordinates of proton i after having made the permutation (123). Figure 1-1 shows the effect of the permutation (123).

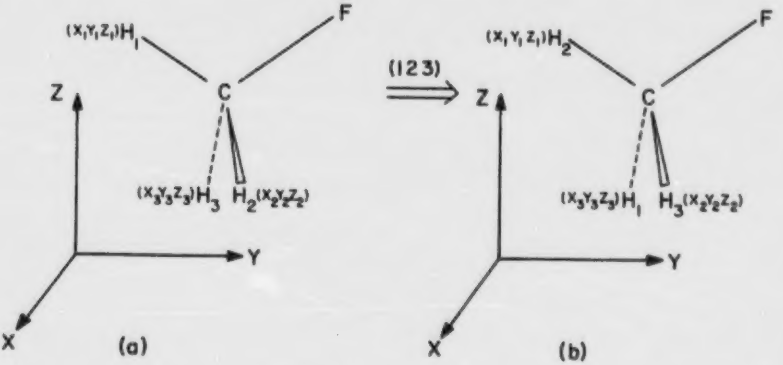

Fig. 1-1. (a) A proton labeled CH_3F molecule with (X, Y, Z) coordinates of H_1, H_2 and H_3 in space given by (X_1, Y_1, Z_1), (X_2, Y_2, Z_2), and (X_3, Y_3, Z_3), respectively. The nuclei H_1, C, and F are in the plane of the page, H_3 is below it and H_2 above it. (b) The same after having performed the permutation (123), i.e., H_1 replaced by H_2, H_2 by H_3, and H_3 by H_1. Now H_2, C, and F are in the plane of the page with H_1 below it and H_3 above it. The coordinates of H_1, H_2, and H_3 are now (X_3, Y_3, Z_3), (X_1, Y_1, Z_1) and (X_2, Y_2, Z_2), respectively.

1.1.1 The effect of a permutation on a function

It is necessary to define the effect of a nuclear permutation operation on a function of the nuclear coordinates (i.e., on a molecular wavefunction). To do this we introduce, as an example, the following function of the X coordinates of the three protons in a CH_3F molecule:

$$f(X_1, X_2, X_3) = X_1 + 2X_2 + 3X_3. \tag{1-14}$$

Using Eq. (1-13) we see that if initially the (X_1, X_2, X_3) nuclear coordinates are (a, b, c) then after applying the permutation (123) they are (c, a, b). The function defined in Eq. (1-14) has the value $a + 2b + 3c$ at the point (a, b, c) in (X_1, X_2, X_3) "space" (called *configuration space*) and the value $c + 2a + 3b$ at the point (c, a, b). The effect of (123) is to change the value of the function at each point (X_1, X_2, X_3) into its value at the point $(X_1', X_2', X_3') = (X_3, X_1, X_2)$. We define the effect of (123) on the function by writing

$$\begin{aligned}(123)f(X_1, X_2, X_3) &= (123)[X_1 + 2X_2 + 3X_3] \\ &= X_1' + 2X_2' + 3X_3' = X_3 + 2X_1 + 3X_2,\end{aligned} \tag{1-15}$$

where we have introduced a new function of the nuclear coordinates, i.e., $X_3 + 2X_1 + 3X_2$. This new function has been defined so that its value at the point

(X_1, X_2, X_3) is the same as the value of the original function, $X_1 + 2X_2 + 3X_3$, at the point $(X_1', X_2', X_3') = (X_3, X_1, X_2)$. We denote this new function by

$$f^{(123)}(X_1, X_2, X_3) = X_3 + 2X_1 + 3X_2, \tag{1-16}$$

and write

$$(123)f(X_1, X_2, X_3) = f^{(123)}(X_1, X_2, X_3). \tag{1-17}$$

With this convention the general equation defining the effect of a permutation P on a function is

$$Pf(X_1, Y_1, Z_1, \ldots, X_l, Y_l, Z_l) = f^P(X_1, Y_1, Z_1, \ldots, X_l, Y_l, Z_l), \tag{1-18}$$

where

$$f^P(X_1, Y_1, Z_1, \ldots, X_l, Y_l, Z_l) = f(X_1', Y_1', Z_1', \ldots, X_l', Y_l', Z_l'), \tag{1-19}$$

and (X_i', Y_i', Z_i') are the coordinates of nucleus i after applying the permutation P. The function $f^P(\,)$ is a new function generated from $f(\,)$ by applying P, and $f^P(\,)$ is such that its value at the point $(X_1, Y_1, Z_1, \ldots, X_l, Y_l, Z_l)$ is the same as the value of $f(\,)$ at the point $(X_1', Y_1', Z_1', \ldots, X_l', Y_l', Z_l')$. Equations (1-18) and (1-19) taken with the equation $P(X_i, Y_i, Z_i) = (X_i', Y_i', Z_i')$, for which examples are given in Eq. (1-10) and (1-13), defines the effect of the nuclear permutation operator P as it is used in this book. This definition is discussed further in the Bibliographical Notes at the end of the chapter.

1.2 THE SUCCESSIVE APPLICATION OF PERMUTATIONS

The solution to Problem 1-1 on page 6 can be represented pictorially as

$$\begin{tikzcd}
\underline{123} \arrow[r, "(23)"] \arrow[rr, bend right, "(13)"'] & \underline{132} \arrow[r, "(132)"] & \underline{321}
\end{tikzcd}$$

This shows how the successive application of first (23) and then (132) to the number order $\underline{123}$ is equivalent to performing the single operation (13); we write

$$(132)(23)\underline{123} = (13)\underline{123}. \tag{1-20}$$

The left hand side of this equation can be expanded as

$$(132)[(23)\underline{123}] = (132)\underline{132} = \underline{321} \tag{1-21}$$

in order to make it clear why we chose to write the operations in the order (132)(23), and not (23)(132), when (23) is applied first. The successive application of first (23) and the (132) to any of the number arrangements in

Eq. (1-1) is always equivalent to the effect of (13), as the reader can verify, and as a result we can write the *operator equation*

$$(132)(23) = (13). \tag{1-22}$$

We say that the *product* of (132) and (23) (or the result of *multiplying* them together) in this order is *equal* (or *equivalent*) to (13); they have the same effect on a number order.

In general the product of two permutations is independent of the number order chosen for the determination of the product [in Eq. (1-20) the number order $\underline{123}$ is used to determine (132)(23)], and with some practice it is possible to determine the product of two permutations without applying them to a number order. As an example let us determine the product (23)(132); this is the same as the product in Eq. (1-22) but taken the other way around. The effect of (132) is to replace 1 by 3, 3 by 2, and 2 by 1; the effect of (23) is then to replace 3 by 2, 2 by 3, and 1 by 1. Overall doing first (132) and then (23) we have the sequences of replacements 1 by 3 by 2, 3 by 2 by 3, and 2 by 1 by 1, i.e., the overall replacements are 1 by 2, 3 by 3, and 2 by 1; this is the effect of (12). Hence

$$(23)(132) = (12). \tag{1-23}$$

Comparing Eqs. (1-22) and (1-23) we see that permutation multiplication is not necessarily commutative, i.e., if A and B are two permutations it is not necessarily true that $AB = BA$.

The multiplication of permutations can be understood using the notation of Eq. (1-5) if we extend that notation a little. We can write Eq. (1-23) as

$$(23)(132) = \begin{pmatrix}123\\132\end{pmatrix}\begin{pmatrix}123\\312\end{pmatrix} = \begin{pmatrix}312\\213\end{pmatrix}\begin{pmatrix}123\\312\end{pmatrix} = \begin{pmatrix}123\\312\\213\end{pmatrix} = \begin{pmatrix}123\\213\end{pmatrix} = (12), \tag{1-24}$$

where the "three-level" parentheses indicate the successive replacements 1 by 3 by 2, 2 by 1 by 1, and 3 by 2 by 3 caused by the successive application of the two permutations.

The reader should now determine the result of multiplying all pairs of distinct permutations from Eq. (1-4) together. Three of the permutation products obtained are

$$(123)(123) = (132), \tag{1-25}$$

$$(12)(23) = (123), \tag{1-26}$$

and

$$(13)(23) = (132). \tag{1-27}$$

From Eqs. (1-26) and (1-27) we see that the cycles can be written as products of transpositions, and it turns out that any permutation can be written as the product of a sequence of transpositions. For example, if we are interested in permuting the first seven integers we can have

$$(15432)(67) = (15)(54)(43)(32)(67). \tag{1-28}$$

In general the breaking down of a permutation into a product of a series of transpositions is not unique, but what is unique is whether there is an odd or even number of transpositions in the product. A permutation is called *even* or *odd* depending on whether there is an even or odd number of transpositions in its transposition product. From Eqs. (1-26) and (1-27) we see that the permutations (123) and (132) are even, and from Eq. (1-28) we see that the permutation (15432)(67) is odd. The importance of determining whether a permutation is even or odd will become apparent when we consider Bose-Einstein and Fermi-Dirac statistical formulas in Chapter 7.

Problem 1-4. Determine whether the following permutations are even or odd: (146)(2357), (17)(23456), (1462357), and (14)(27)(36).

Answer. We can write these permutation in many ways as the product of transpositions but one possible way for each is now given:

$$\begin{aligned}(146)(2357) &= (14)(46)(23)(35)(57),\\ (17)(23456) &= (17)(23)(34)(45)(56),\\ (1462357) &= (14)(46)(62)(23)(35)(57),\\ (14)(27)(36) &= (14)(27)(36).\end{aligned} \tag{1-29}$$

The third one is even and the rest are odd. A cycle that permutes n numbers is even (odd) if $(n-1)$ is even (odd).

It is presumed that on multiplying all the permutations of Eq. (1-4) together in pairs the reader will have attempted

$$(123)(132) = \ ? \tag{1-30}$$

and have wondered about what to give as the answer. Obviously doing first (132) and then (123) has the overall effect of leaving the number order unchanged, and we simply have to invent a symbol to mean "doing nothing" (the equivalent of 1 in algebraic multiplication). The symbol we use is E and we write

$$(123)(132) = E. \tag{1-31}$$

Also we can write equations such as

$$(12)E = (12). \tag{1-32}$$

E is called the ***identity operation***.

Having defined the identity operation we can now define the *reciprocal*, or *inverse*, of an operation. We define the reciprocal of an operation A, say, as that operation which when multiplied on the right of A gives the identity. For example (132) is the reciprocal of (123) from the result in Eq. (1-31); i.e.,

$$(123)(123)^{-1} = E \tag{1-33}$$

defines $(123)^{-1}$, and from Eq. (1-31) we have

$$(123)^{-1} = (132). \tag{1-34}$$

Similarly

$$(132)^{-1} = (123), \tag{1-35}$$

and all the transpositions are self-reciprocal, i.e.,

$$(12)^{-1} = (12), \tag{1-36}$$

$$(23)^{-1} = (23), \tag{1-37}$$

and

$$(13)^{-1} = (13). \tag{1-38}$$

Using the notation of Eq. (1-5) the inverse of a permutation is obtained by simply turning the permutation "upside down," that is,

$$\begin{aligned}(abcd\cdots xyz)^{-1} = \begin{pmatrix} abc\cdots xyz \\ bcd\cdots yza \end{pmatrix}^{-1} &= \begin{pmatrix} bcd\cdots yza \\ abc\cdots xyz \end{pmatrix} \\ &\equiv \begin{pmatrix} azy\cdots dcb \\ zyx\cdots cba \end{pmatrix} \\ &= (azyx\cdots dcb). \end{aligned} \tag{1-39}$$

Hence, for example, we have,

$$(1423756)^{-1} = (1657324). \tag{1-40}$$

Problem 1-5. Determine the effect of the successive applications of first (132) and then (23) on the coordinates of the three protons in CH_3F and on the function $[X_1 + 2X_2 + 3X_3]$.

Answer. The effect of the successive application of these permutations on the proton coordinates is best understood by using the notation of Eqs. (1-8) and (1-11). In this case we write

$$
\begin{aligned}
&(23)(132)[\underbrace{X_1, Y_1, Z_1}_{\textcircled{1}}, \underbrace{X_2, Y_2, Z_2}_{\textcircled{2}}, \underbrace{X_3, Y_3, Z_3}_{\textcircled{3}}] \\
&= (23)[\underbrace{X_1, Y_1, Z_1}_{\textcircled{3}}, \underbrace{X_2, Y_2, Z_2}_{\textcircled{1}}, \underbrace{X_3, Y_3, Z_3}_{\textcircled{2}}] \\
&= [\underbrace{X_1, Y_1, Z_1}_{\textcircled{2}}, \underbrace{X_2, Y_2, Z_2}_{\textcircled{1}}, \underbrace{X_3, Y_3, Z_3}_{\textcircled{3}}]. \qquad (1\text{-}41)
\end{aligned}
$$

Thus proton 3 ends up in the same place in space as it started and protons 1 and 2 are interchanged; this is in accordance with Eq. (1-23). A function such as $[X_1 + 2X_2 + 3X_3]$, which is to be read as "the X coordinate of proton 1 plus twice the X coordinate of proton 2 plus three times the X coordinate of proton 3," transforms under (23)(132) as

$$
\begin{aligned}
(23)(132)[X_1 + 2X_2 + 3X_3] &= (23)[X_2 + 2X_3 + 3X_1] \\
&= [X_2 + 2X_1 + 3X_3]. \qquad (1\text{-}42)
\end{aligned}
$$

After applying (132) the X coordinates of protons 1, 2, and 3 are X_2, X_3, and X_1, respectively so that (23) permutes X_3 and X_1 in the function (the coordinates of 2 and 3). This is perhaps better understood if we introduce the notation that X_i' is the X coordinate of proton i after having applied (132) so that

$$
\begin{aligned}
(23)(132)[X_1 + 2X_2 + 3X_3] &= (23)[X_1' + 2X_2' + 3X_3'] \\
&= [X_1' + 2X_3' + 3X_2'] \\
&= [X_2 + 2X_1 + 3X_3]. \qquad (1\text{-}43)
\end{aligned}
$$

We see that if

$$f(X_1, X_2, X_3) = X_1 + 2X_2 + 3X_3,$$

then

$$f^{(23)(132)}(X_1, X_2, X_3) = X_2 + 2X_1 + 3X_3, \qquad (1\text{-}44)$$

and

$$f^{(23)(132)}(X_1, X_2, X_3) = f^{(12)}(X_1, X_2, X_3). \qquad (1\text{-}45)$$

1.3 THE DEFINITION OF A GROUP

By considering all permutations of the integers 1, 2, and 3, and the results of all possible products of them, we have constructed the following set of distinguishable permutation operations:

$$\{E, (12), (23), (13), (123), (132)\}. \tag{1-46}$$

Having defined how to multiply these operations together in pairs we can construct the *multiplication table* of this set of elements and this is given in Table 1-1. In Table 1-1 each entry C represents the result of first applying the operation B at the head of its column and then applying the operation A at the beginning of its row, i.e., $C = AB$. The set of operations in Eq. (1-46) is, in fact, a *group* because it satisfies the following *group axioms*:

1. We can multiply (i.e., successively apply) the operations (or elements) together in pairs and the result is a member of the group.
2. One of the operations in the group is the identity operation E.
3. The reciprocal of each operation is a member of the group.
4. Multiplication of the operations is associative; that is, in a multiple product the answer is independent of how the operations are associated in pairs, e.g.,

$$(12)(123)(23) = (12)\underbrace{[(123)(23)]}_{(12)} = \underbrace{[(12)(123)]}_{(23)}(23) = E. \tag{1-47}$$

The fact that the group axioms 1, 2, 3, and 4 are satisfied by the set in Eq. (1-46) can be verified by inspecting the multiplication table (Table 1-1), and thus the set is a group. We will generally enclose the members of a group in braces { }.

Table 1-1

The multiplication table of the S_3 group[a]

	E	(12)	(23)	(13)	(123)	(132)
E:	E	(12)	(23)	(13)	(123)	(132)
(12):	(12)	E	(123)	(132)	(23)	(13)
(23):	(23)	(132)	E	(123)	(13)	(12)
(13):	(13)	(123)	(132)	E	(12)	(23)
(123):	(123)	(13)	(12)	(23)	(132)	E
(132):	(132)	(23)	(13)	(12)	E	(123)

[a] Each entry is the product of first applying the permutation at the top of the column and then applying the permutation at the left end of the row.

This particular group is called S_3, the permutation group (or symmetric group) of degree 3, and it consists of all permutations of three objects. There are six elements in $\boldsymbol{S}_3$ and the group is said to have *order* six. In general, the permutation group $\boldsymbol{S}_n$ (all permutations of n objects) has order $n!$. Factorials grow very quickly so that, for example, $60! = 832098711274139014427634118322336$ $4380754172606361245952449277696409600000000000000$. We have used the program system MAPLE [see, for example, Monagan, Geddes, Labahn, and Vorkoetter (1996)] to evaluate this factorial.

Problem 1-6. Prove that if $AB = E$, i.e., $A^{-1} = B$ from Eq. (1-33), then $BA = E$, i.e., $B^{-1} = A$ also, if A and B are in a group. (Hint: Evaluate BAB two different ways using axiom 4.)

Answer. The triple product BAB can be evaluated as $B[AB]$ or $[BA]B$. The first way of associating the elements gives the answer $BE = B$, since $AB = E$. The second way of associating the elements must give the same answer (by group axiom 4), i.e., $[BA]B = B$. This can only be true if $BA = E$ which was what we set out to prove. In $\boldsymbol{S}_3$ we have, for example,

$$(123)(132) = (132)(123) = E. \tag{1-48}$$

Axiom 4 can be used to prove that

$$(AB)^{-1} = B^{-1}A^{-1}. \tag{1-49}$$

We can write

$$(AB)(B^{-1}A^{-1}) = A(BB^{-1})A^{-1} = AEA^{-1} = AA^{-1} = E, \tag{1-50}$$

but

$$(AB)(AB)^{-1} = E, \tag{1-51}$$

thus

$$(AB)^{-1} = B^{-1}A^{-1}.$$

In general the reciprocal of a product is the product of the reciprocals taken in the reverse order, e.g.,

$$(ABCD)^{-1} = D^{-1}C^{-1}B^{-1}A^{-1}. \tag{1-52}$$

Problem 1-7. Three of the elements of $\boldsymbol{S}_3$ taken by themselves satisfy the group axioms and hence form a group. Which three elements are they? Such a group is called a ***subgroup*** of the $\boldsymbol{S}_3$ group.

Answer. It is clear that E has to be in the subgroup in order for it to form a group (by axiom 2). Perhaps the set $\{E, (12), (23)\}$ is a subgroup? This set satisfies axiom 3 by virtue of Eqs. (1-36) and (1-37). However, $(12)(23) = (123)$, and (123) is not in the set; thus by axiom 1 this set is not a group. By studying Table 1-1 the subgroup is found to be $\{E, (123), (132)\}$.

The only condition for a subset of the elements of a group to form a subgroup is that the subset contain all products of its members. The subgroup discussed in Problem 1-7 has order 3 and it is called an ***Abelian group*** since multiplication within it is commutative [see the first equality in Eq. (1-48)]. Other subgroups of $\boldsymbol{S}_3$ are $\{E, (12)\}$, $\{E, (23)\}$, and $\{E, (13)\}$, each having order 2, and $\{E\}$ of order 1.

1.4 THE COMPLETE NUCLEAR PERMUTATION (CNP) GROUP OF A MOLECULE

Labeling the protons in the CH_3F molecule as 1, 2, and 3, the group $\boldsymbol{S}_3$ of Eq. (1-46) contains all possible permutations of identical nuclei in the molecule. We call this group the *complete nuclear permutation* (CNP) group of the CH_3F molecule. The CNP group of a molecule having n identical nuclei of one type, and no sets of other identical nuclei, will be the group $\boldsymbol{S}_n$ of permutations of these nuclei.

If a molecule has more than one set of identical nuclei the definition of the CNP group is more complicated and we will illustrate this by considering the ethylene molecule C_2H_4. Labeling the protons in the molecule 1 to 4, the group of all proton permutations is the group $\boldsymbol{S}_4$. Numbering the carbon nuclei 5 and 6 the group of all carbon nuclei permutations is the group $\boldsymbol{S}_2 = \{E, (56)\}$. We will denote these two nuclear permutation groups $\boldsymbol{S}_4^{(\mathrm{H})}$ and $\boldsymbol{S}_2^{(\mathrm{C})}$. The group of all possible permutations of identical nuclei in the molecule (the CNP group) will therefore consist of all 4! elements of the group $\boldsymbol{S}_4^{(\mathrm{H})}$ *and* of all these elements taken in combination with (56); 2 × 4! elements in all. The element (56) will commute with all the elements of the $\boldsymbol{S}_4^{(\mathrm{H})}$ group, since these two groups involve permutations of different types of nuclei. This CNP group is called the *direct product* of the groups $\boldsymbol{S}_4^{(\mathrm{H})}$ and $\boldsymbol{S}_2^{(\mathrm{C})}$ and is written

$$\boldsymbol{G}^{\mathrm{CNP}} = \boldsymbol{S}_4^{(\mathrm{H})} \otimes \boldsymbol{S}_2^{(\mathrm{C})}. \tag{1-53}$$

In general the direct product of a group $\boldsymbol{A} = \{A_1 \equiv E, A_2, \ldots, A_n\}$ and a group $\boldsymbol{B} = \{B_1 \equiv E, B_2, \ldots, B_m\}$, where all A_i commute with all B_j, is the set of $n \times m$ elements $A_iB_j (= B_jA_i)$ where $i = 1$ to n and $j = 1$ to m. One element in this set, the element A_1B_1, will be the identity, and the product of any two elements in the set will give another element of the set. This latter result follows by considering

$$(A_iB_j)(A_kB_l) = A_iA_kB_jB_l = A_pB_q, \tag{1-54}$$

where

$$A_p = A_iA_k \qquad \text{in the group } \boldsymbol{A},$$
$$B_q = B_jB_l \qquad \text{in the group } \boldsymbol{B},$$

and A_pB_q must be in the set of direct product elements since it is defined to contain all products. The inverse of each element is present since

$$(A_iB_j)^{-1} = B_j^{-1}A_i^{-1} \tag{1-55}$$

and B_j^{-1} is an element in $\boldsymbol{B}$ and A_i^{-1} in $\boldsymbol{A}$, since $\boldsymbol{A}$ and $\boldsymbol{B}$ are groups. The associative law of multiplication must hold for the direct product elements since it holds within the groups $\boldsymbol{A}$ and $\boldsymbol{B}$. Thus the set of $n \times m$ elements A_iB_j

forms a group and it is called the direct product group. In this definition it is crucial that each element in $\boldsymbol{A}$ commute with each element in $\boldsymbol{B}$.

The CNP group of a molecule containing l identical nuclei of one set, m of another, n of another, and so on, is the direct product group

$$\boldsymbol{G}^{\mathrm{CNP}} = \boldsymbol{S}_l \otimes \boldsymbol{S}_m \otimes \boldsymbol{S}_n \otimes \cdots , \tag{1-56}$$

and the order of the group is $l! \times m! \times n! \times \cdots$. Group products are discussed further in Section 5.7.

Problem 1-8. Write down the elements of the CNP group of the molecule CHOCOOH.

Answer. The CNP group is the direct product group

$$\begin{aligned} \boldsymbol{G}^{\mathrm{CNP}} &= \boldsymbol{S}_3^{(\mathrm{O})} \otimes \boldsymbol{S}_2^{(\mathrm{H})} \otimes \boldsymbol{S}_2^{(\mathrm{C})} \\ &= \{E, (12), (23), (13), (123), (132)\} \otimes \{E, (45)\} \otimes \{E, (67)\}, \end{aligned} \tag{1-57}$$

where we label the oxygen nuclei 1, 2, and 3; the protons 4 and 5; the carbon nuclei 6 and 7. The complete list of ($3! \times 2! \times 2! = 24$) elements is

$$\begin{aligned} &\{E, (12), (23), (13), (123), (132), \\ &(45), (12)(45), (23)(45), (13)(45), (123)(45), (132)(45), \\ &(67), (12)(67), (23)(67), (13)(67), (123)(67), (132)(67), (45)(67) \\ &(12)(45)(67), (23)(45)(67), (13)(45)(67), (123)(45)(67), (132)(45)(67)\}. \end{aligned} \tag{1-58}$$

Problem 1-9. We label the protons of an ethylene molecule 1 to 4, and the carbon nuclei 5 and 6 as shown in Fig. 1-2. There are 11 other distinct ways of putting the labels 1 to 6 on the nuclei so that the protons are labeled 1 to 4 and the carbon nuclei 5 and 6; write down these other distinct ways (distinct means those not simply obtained by rigidly rotating the molecule in space). If we only include permutations from the CNP group of ethylene that do not convert our chosen labeled form into any of the other 11 forms which set of permutations is obtained? Prove that this set of permutations forms a group.

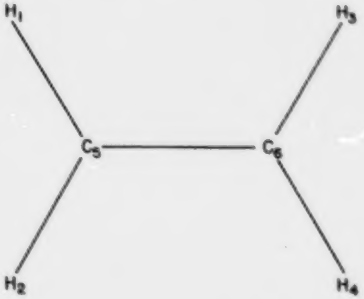

Fig. 1-2. An ethylene molecule with the nuclei labeled 1 to 6.

Answer. The twelve distinct nuclear labeled forms of ethylene are shown in Fig. 1-3. The set of permutations that does not convert the form in Fig. 1-3a into any other form is

$$\{E, (12)(34), (13)(24)(56), (14)(23)(56)\}, \tag{1-59}$$

and this set is a group, a subgroup of the CNP group, since any product of the elements of the set gives an element that is in the set.

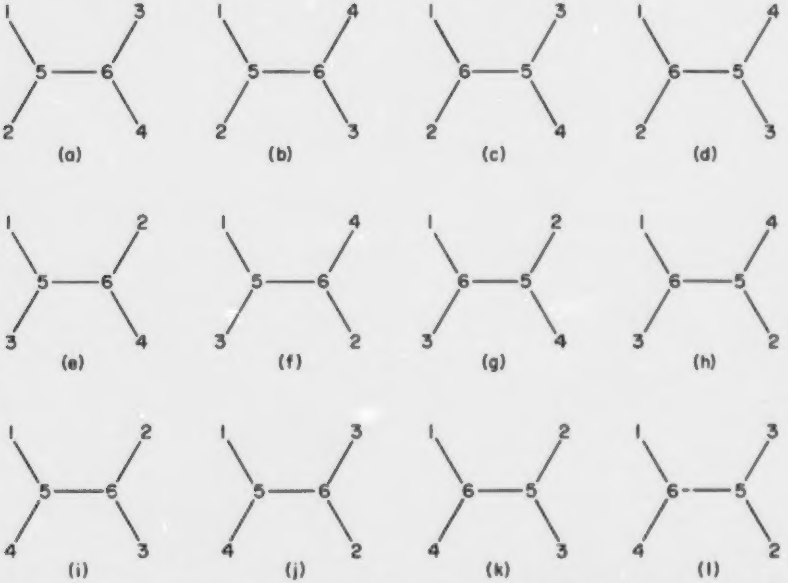

Fig. 1-3. The 12 distinct forms of an ethylene molecule in which the protons are labeled 1 to 4 and the carbon nuclei 5 to 6. Distinct forms cannot be interconverted by simply rigidly rotating them in space.

In Problem 1-9 we obtained a subgroup of the CNP group of the ethylene molecule by considering only elements that do not interconvert some distinct nuclear labeled forms of the molecule. Notice that the subgroup of $\boldsymbol{S}_3$, of order 3, obtained as answer to Problem 1-7 on page 15, contains all elements of the CNP group of CH_3F that do not interconvert the two distinct (clockwise and anticlockwise) labeled forms of the molecule. The idea of distinct nuclear labeled forms (called *versions*) of a molecule, and of a subgroup of elements that does not interconvert them will prove to be very important when we come to define the molecular symmetry group in Chapter 3. Complete electron permutation groups will not be discussed very much in this book, although their use in electronic structure calculations is briefly explained in Section 9.4.5.

BIBLIOGRAPHICAL NOTES

Wigner (1959). Permutations are discussed on pages 64-65 and on pages 124-127. A group is defined on pages 58-59. The effect of an operation on a function is discussed on pages 104-106. Different definitions from those adopted here are used for the effect of a permutation on coordinates and functions.

Bunker and Howard (1983). The implications of using the definition adopted here for the effect of a permutation on coordinates and functions, rather than the definition used in Wigner (1959), are fully discussed. We summarize the important point of this paper here. To explain the approach used in Wigner's book (called W) we introduce three positions in space labeled $\underline{1}$, $\underline{2}$ and $\underline{3}$ as well as three nuclei labeled 1, 2 and 3. In W the permutation $(12)^W$ (the superscript W is used to distinguish it from the permutation (12) as defined in the present chapter) is defined as exchanging the nuclei in positions $\underline{1}$ and $\underline{2}$, and $(132)^W$ as the operation that replaces the nucleus in position $\underline{1}$ by that in position $\underline{3}$, that in position $\underline{3}$ by that in position $\underline{2}$, and that in position $\underline{2}$ by that in position $\underline{1}$. If we initially start with nuclei 1, 2, and 3 in positions $\underline{1}$, $\underline{2}$, and $\underline{3}$ respectively then the effect of doing $(132)^W$ followed by $(12)^W$ is:

$$\begin{tikzcd}
\begin{matrix}123\\ \underline{123}\end{matrix} \arrow[r, "(132)^W"] \arrow[rr, bend right, "(23)^W"'] & \begin{matrix}312\\ \underline{123}\end{matrix} \arrow[r, "(12)^W"] & \begin{matrix}132\\ \underline{123}\end{matrix}
\end{tikzcd}$$

Thus, in agreement with the expression for P_1P_2 on page 64 of W, we deduce that

$$(12)^W(132)^W = (23)^W. \tag{1-60}$$

In the approach of the present chapter we have

$$(12)(132) = (13). \tag{1-61}$$

Also in W the effect of a permutation on a function is defined in a way that differs from our Eq. (1-19). These differing definitions have important implications when we come to apply groups to molecules and this is discussed further in the Bibliographical Notes of Chapter 6 concerning Wigner (1959).

2

The Complete Nuclear Permutation Inversion Group

The inversion operation E^* is defined and its effect on a molecule, and on a molecular wavefunction, is discussed; its use allows us to determine the parity of a molecular wavefunction. The effect of the successive application of E^* and of a nuclear permutation operation is also considered, and as a result we are able to define the complete nuclear permutation inversion (CNPI) group of a molecule. The detailed effect of an element of the group on the coordinates of the nuclei and electrons in a molecule is presented.

2.1 THE INVERSION OPERATION E^* AND PARITY

As well as permuting the coordinates of identical nuclei it is necessary to consider the effect of inverting the spatial coordinates of all particles (nuclei and electrons) in a molecule through the origin of the space fixed axis system. This operation involves changing the sign of the Cartesian coordinates in space of all the particles in the molecule. Since the translational motion of a molecule will not be of any concern to us, it will prove convenient to refer the coordinates of the electrons and nuclei to the molecular center of mass; this involves the separation of the translational motion, which will be discussed more fully in Chapter 7. From now on when we discuss the spatial coordinates of the nuclei and electrons in a molecule we will usually use an (X, Y, Z) axis system parallel to the space fixed (X, Y, Z) axis system but with origin at the molecular center of mass. The inversion operation E^*, when applied to a molecule, is defined as the operation of inverting the spatial coordinates of all the nuclei and electrons through the molecular center of mass. Using the (X, Y, Z) coordinates of a nucleus or electron we can write

$$E^*[X_i, Y_i, Z_i] = [X_i', Y_i', Z_i'] = [-X_i, -Y_i, -Z_i]. \qquad (2\text{-}1)$$

Problem 2-1. Write down the effect of E^* on the spatial coordinates of the five nuclei in a CH_3F molecule. Draw a picture of a CH_3F molecule and draw the effect of E^*.

Answer. By definition E^* simply changes the sign of the (X, Y, Z) coordinates of all the nuclei, i.e.,

$$E^*[X_1, Y_1, Z_1, \ldots, X_F, Y_F, Z_F] = [-X_1, -Y_1, -Z_1, \ldots, -X_F, -Y_F, -Z_F]. \tag{2-2}$$

In Fig. 2-1a a methyl fluoride molecule is arbitrarily oriented with its center of mass at the origin of the (X, Y, Z) axis system. The operation E^* inverts the coordinates of all particles in the origin of the (X, Y, Z) system, and the result is shown in Fig. 2-1b; the (X, Y, Z) axis system is unaffected by E^* by definition. In Fig. 2-2 the effect of E^* is given without showing the (X, Y, Z) axes and in our figures the axes will often be omitted. Figures 2-1 and 2-2 are simply pictorial representations of Eq. (2-2). Although not mentioned in Eq. (2-2) and not explicitly shown in Figs. 2-1 and 2-2, the coordinates of the electrons are also inverted by E^*.

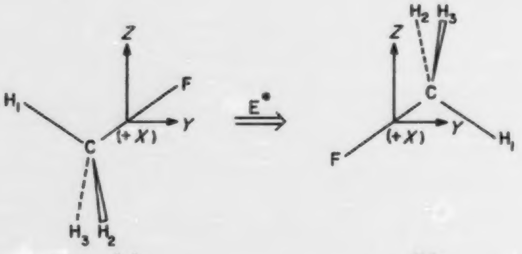

Fig. 2-1. The effect of E^* on a CH_3F molecule. The $(+X)$ indicates that the X axis is pointing up out of the plane of the page.

We define the effect of E^* on a function of the nuclear and electronic coordinates in the same way as we did for a nuclear permutation in Eq. (1-18) and (1-19), i.e.,

$$E^* f(X_1, Y_1, Z_1, \ldots, X_n, Y_n, Z_n) = f^{E^*}(X_1, Y_1, Z_1, \ldots, X_n, Y_n, Z_n), \tag{2-3}$$

and

$$f^{E^*}(X_1, Y_1, Z_1, \ldots, X_n, Y_n, Z_n) = f(-X_1, -Y_1, -Z_1, \ldots, -X_n, -Y_n, -Z_n). \tag{2-4}$$

The value of the new function $f^{E^*}()$ at each point $(X_1, Y_1, Z_1, \ldots)$ is the same as the value of the original function $f()$ at each point $(-X_1, -Y_1, -Z_1, \ldots)$.

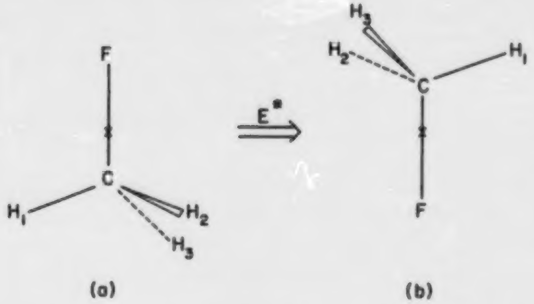

Fig. 2-2. The effect of E^* on CH_3F without drawing the space fixed axes.

If a function $f()$ is such that its values at the points $(X_1, Y_1, Z_1, \ldots)$ and $(-X_1, -Y_1, -Z_1, \ldots)$ are the same then

$$f^{E^*}(\ ) = f(\ ) \tag{2-5}$$

and the function is said to have *positive parity*. If on the other hand the values of the function at the points $(X_1, Y_1, Z_1, \ldots)$ and $(-X_1, -Y_1, -Z_1, \ldots)$ are the negative of each other then

$$f^{E^*}(\ ) = -f(\ ) \tag{2-6}$$

and the function has *negative parity*. For a function of positive parity we can write

$$E^* f(\ ) = f(\ ), \tag{2-7}$$

and for a function of negative parity we can write

$$E^* f(\ ) = -f(\ ). \tag{2-8}$$

2.2 COMBINING PERMUTATIONS WITH THE INVERSION: THE CNPI GROUP

Figure 2-2 shows the effect of the inversion operation E^* on a methyl fluoride molecule. We could easily apply a permutation operation, (12) say, after doing E^* (i.e., to Fig. 2-2b), and the resulting combined operation would be written $(12)E^*$. The effect of $(12)E^*$ on the coordinates of the nuclei is given by

$$\begin{aligned}(12)E^*[X_1, Y_1, Z_1, X_2, Y_2, Z_2, X_3, Y_3, Z_3, X_C, Y_C, Z_C, X_F, Y_F, Z_F]\\ = [-X_2, -Y_2, -Z_2, -X_1, -Y_1, -Z_1, -X_3, -Y_3, -Z_3,\\ -X_C, -Y_C, -Z_C, -X_F, -Y_F, -Z_F].\end{aligned} \tag{2-9}$$

The effect of a permutation operation P is to interchange the nuclear coordinates, and the inversion changes the sign of all coordinates. It is clearly immaterial whether we change the sign of the coordinates with E^* before or after interchanging them with P, and thus E^* and P will commute. We can write

$$(12)E^* = E^*(12) = (12)^*, \tag{2-10}$$

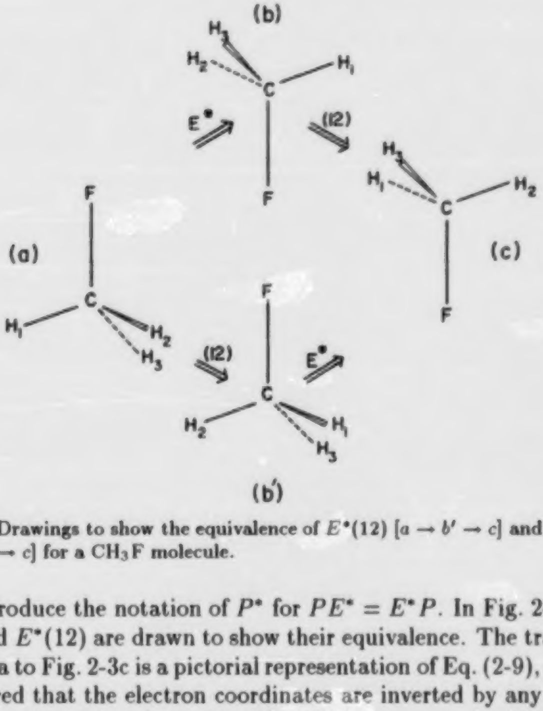

Fig. 2-3. Drawings to show the equivalence of $E^*(12)$ $[a \rightarrow b' \rightarrow c]$ and $(12)E^*$ $[a \rightarrow b \rightarrow c]$ for a CH_3F molecule.

where we introduce the notation of P^* for $PE^* = E^*P$. In Fig. 2-3 the results of $(12)E^*$ and $E^*(12)$ are drawn to show their equivalence. The transformation from Fig. 2-3a to Fig. 2-3c is a pictorial representation of Eq. (2-9), and it should be remembered that the electron coordinates are inverted by any permutation inversion operation P^* such as this. We will be concerned with the effects of both P and P^* operations on nuclear and electron coordinates and on functions of the coordinates.

Problem 2-2. By drawing pictures such as Fig. 2-3 verify that E^* commutes with all the elements of the complete nuclear permutation group of CH_3F, where this group is

$$S_3^{(H)} = \{E, (12), (23), (13), (123), (132)\}. \tag{2-11}$$

Which of the operations in the direct product group $S_3^{(H)} \otimes \{E, E^*\}$, i.e., the group

$$\{E, (12), (23), (13), (123), (132), E^*, (12)^*, (23)^*, (13)^*, (123)^*, (132)^*\}, \tag{2-12}$$

does not interconvert clockwise and anticlockwise labeled CH_3F?

Answer. The set of operations that does not interconvert the clockwise and anticlockwise labeled forms is the group

$$\{E, (123), (132), (12)^*, (23)^*, (13)^*\}. \tag{2-13}$$

For reasons that will emerge we call this group $\boldsymbol{C}_{3v}(M)$.

The group in Eq. (2-12) is called the ***complete nuclear permutation inversion*** (CNPI) group of CH_3F; the CNPI group of a given molecule contains all possible permutations of identical nuclei in the molecule with and without inversion. The CNPI group of a molecule is the direct product of the complete nuclear permutation group [as introduced in Eq. (1-56)] and the ***inversion group*** $\mathcal{E} = \{E, E^*\}$; the CNPI group contains twice as many elements as the complete nuclear permutation group.

The group in Eq. (2-13) is the molecular symmetry group of the CH_3F molecule in its ground electronic state. The definition of the molecular symmetry group will be discussed in Chapter 3.

Problem 2-3. What is the complete nuclear permutation inversion group of the ethylene molecule using the nuclear labeling convention of Fig. 1-2 on page 17? Which of the elements do not convert the form in Fig. 1-3a on page 18 into any of the other 11 distinct nuclear labeled forms of Fig. 1-3?

Answer. The complete nuclear permutation inversion group is the direct product

$$\boldsymbol{S}_4^{(H)} \otimes \boldsymbol{S}_2^{(C)} \otimes \mathcal{E}, \tag{2-14}$$

and it has $4! \times 2! \times 2 = 96$ elements. Typical elements are (132), (13)(56), (1234)(56), $(12)(34)^*$, $(124)(56)^*$, etc. The subgroup that does not convert the form in Fig. 1-3a into any of the other distinct nuclear labeled forms is

$$\begin{aligned}\{E, (12)(34), (13)(24)(56), (14)(23)(56), E^*, (12)(34)^*,\\ (13)(24)(56)^*, (14)(23)(56)^*\},\end{aligned} \tag{2-15}$$

and this is called the molecular symmetry group of the rigidly planar ethylene molecule; it is named $\boldsymbol{D}_{2h}(M)$. Because E^* commutes with permutations we can write, for example,

$$(12)(34)^* = (12)(34)E^* = (12)E^*(34) = E^*(12)(34) = (12)^*(34). \tag{2-16}$$

Problem 2-4. Draw the effect of applying $(12)(34)^*$ and (13)(24)(56) to the ethylene molecule in Fig. 1-2 on page 17. Is there any difference between the effects of these operations?

Answer. Yes. If the nuclei of the ethylene molecule are in the equilibrium configuration (as they are in Fig. 1-2) then $(12)(34)^*$ and (13)(24)(56) have the same effect on the nuclear coordinates, but $(12)(34)^*$ inverts the electron coordinates whereas (13)(24)(56) does not. If the nuclei are not in the equilibrium configuration then the effects of these operations on the nuclear coordinates will usually be different, and this is discussed in more detail in the next section.

2.3 THE DETAILED EFFECTS OF P AND P^* OPERATIONS

In the preceding section we have discussed the effect of a nuclear permutation operation P, and the effect of a nuclear permutation operation accompanied by an inversion, P^*, several times. However, in the figures we have always considered the molecule to be in its equilibrium configuration. This was not necessary but it made it easier to draw the figures. Also we have given figures *and* equations, and it is a good idea to use both in order to have a full understanding of and ability to use the molecular symmetry group. In this section we are going to look at the effect of each of the two operations used in Problem 2-4 in more detail, both with figures and equations, and we are going to apply them to an ethylene molecule that is not in its equilibrium configuration.

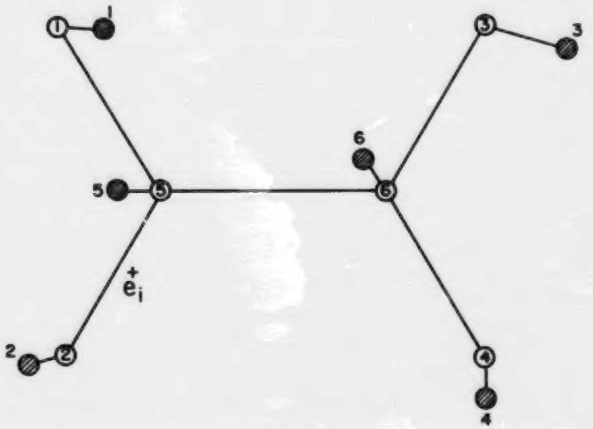

Fig. 2-4. An ethylene molecule. The shaded circles represent an instantaneous nuclear arrangement (i.e., a "snapshot" of the rotating-vibrating molecule), and the open circles the appropriate equilibrium nuclear arrangement. $\overset{+}{e}_i$ represents an electron i above the plane of the page.

In Fig. 2-4 the shaded circles show the instantaneous positions of the four hydrogen nuclei and two carbon nuclei in an ethylene molecule that is rotating and vibrating in space; the open circles show the appropriate equilibrium nuclear positions, and $\overset{+}{e}_i$ represents electron i above the plane of the page ($\bar{e}_i$ would represent electron i below the plane of the page). For simplicity we have chosen to keep all the nuclei in the plane of the page. We can write the instantaneous coordinates of the nuclei and electrons in the space fixed (X, Y, Z) axis system (the origin is at the common center of mass of the instantaneous and equilibrium configuration molecules) as $[X_1, Y_1, Z_1, \ldots, X_6, Y_6, Z_6; X_i, Y_i, Z_i]$, where the electrons are labeled i.

We wish to consider the effects of the operations $(12)(34)^*$ and $(13)(24)(56)$ of the molecular symmetry group of ethylene. Equation (2-17) and Fig. 2-5 show the effect of the (12)(34)*, and Eq. (2-18) and Fig. 2-6 show the effect of (13)(24)(56), on the nuclear and electronic coordinates.

$$\begin{aligned}(12)(34)^*[X_1, Y_1, Z_1, X_2, Y_2, Z_2, X_3, Y_3, Z_3, X_4, Y_4, Z_4, X_5, Y_5, Z_5,\\ X_6, Y_6, Z_6; X_i, Y_i, Z_i] = [-X_2, -Y_2, -Z_2, -X_1, -Y_1, -Z_1,\\ -X_4, -Y_4, -Z_4, -X_3, -Y_3, -Z_3,\\ -X_5, -Y_5, -Z_5, -X_6, -Y_6, -Z_6;\\ -X_i, -Y_i, -Z_i],\end{aligned} \qquad (2\text{-}17)$$

and

$$\begin{aligned}(13)(24)(56)[X_1, Y_1, Z_1, X_2, Y_2, Z_2, X_3, Y_3, Z_3, X_4, Y_4, Z_4, X_5, Y_5, Z_5,\\ X_6, Y_6, Z_6; X_i, Y_i, Z_i] = [X_3, Y_3, Z_3, X_4, Y_4, Z_4, X_1, Y_1, Z_1,\\ X_2, Y_2, Z_2, X_6, Y_6, Z_6, X_5, Y_5, Z_5;\\ X_i, Y_i, Z_i].\end{aligned} \qquad (2\text{-}18)$$

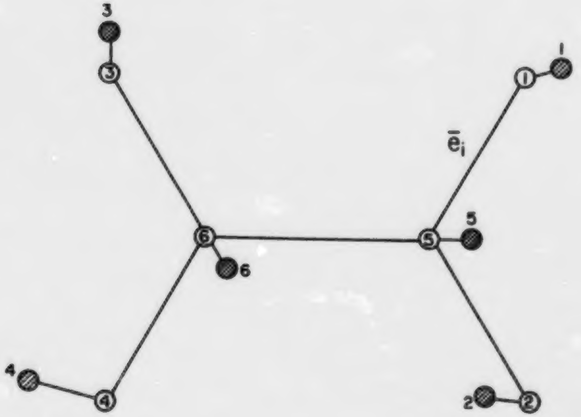

Fig. 2-5. The effect of applying the operation (12)(34)* to the ethylene molecule of Fig. 2-4, $\bar{e}_i$ represents electron i below the plane of the page.

If the molecule were in its equilibrium configuration then because of the centrosymmetric nature of the molecule we would have

$$\begin{gathered}X_1 = -X_4, \quad Y_1 = -Y_4, \quad Z_1 = -Z_4, \quad X_2 = -X_3, \quad Y_2 = -Y_3,\\ Z_2 = -Z_3, \quad X_5 = -X_6, \quad Y_5 = -Y_6 \quad \text{and} \quad Z_5 = -Z_6,\end{gathered} \qquad (2\text{-}19)$$

so that the effects of (12)(34)* and (13)(24)(56) on the nuclear coordinates would be the same. This can be seen by inserting Eq. (2-19) into the right hand side of Eq. (2-17) and comparing with Eq. (2-18), or by looking at the positions of the open circles in Figs. 2-5 and 2-6. The electronic coordinates are inverted by (12)(34)* but not by (13)(24)(56).

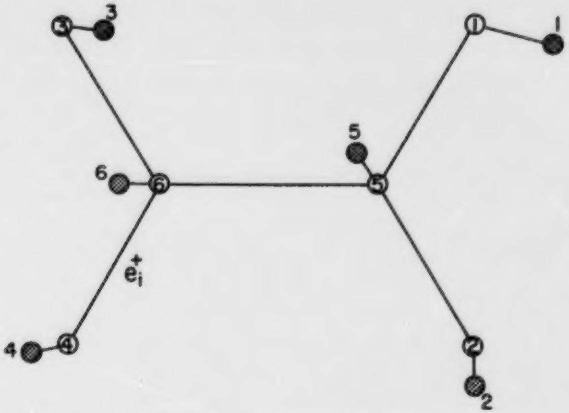

Fig. 2-6. The effect of applying the operation (13)(24)(56) to the ethylene molecule of Fig. 2-4.

2.4 SUMMARY

In this chapter and the previous one the complete nuclear permutation (CNP) group and the complete nuclear permutation inversion (CNPI) group of a molecule have been defined. The effects of the elements of these groups, and of products of these elements, on nuclear and electronic coordinates in space (and on functions of these coordinates) has been explained.

BIBLIOGRAPHICAL NOTES

Hougen (1963). This paper shows how the inversion operation that is now called E^* [following Longuet-Higgins (1963)] is dealt with in discussing the transformation properties of molecular coordinates.

3

The Molecular Symmetry Group

The molecular symmetry group is defined. In a preamble we outline the way that groups are used in molecular physics, and point out that we could use the CNPI group as defined in Chapter 2. However, there are drawbacks, and we show how the use of a subgroup, which is the molecular symmetry group, overcomes these drawbacks. We define the terms rigid and nonrigid molecule, and give examples of molecular symmetry groups for them. We include a special discussion of weakly bound cluster molecules, sometimes called 'van der Waals molecules'.

3.1 PREAMBLE

This is a summary of results that will be developed later.

Every group has a specific set of *irreducible representations* with names such as A_1, B_g, E', and F_2 (Chapter 5). In the same way as we label a state according to its parity by determining the effect of E^* on the wavefunction of the state [see Eqs. (2-3)-(2-8)], we can label a state according to the irreducible representations of a *symmetry group* of the molecule in question by determining the effect of the elements of the group on the wavefunction (Chapter 6). A symmetry group of a molecule is a group whose elements commute with the Hamiltonian of the molecule; using somewhat looser language the elements of a symmetry group of a molecule do not change the energy of the molecule. This does not seem to have anything to do with the customary use of the word 'symmetry' which is concerned with the geometrical shape of an object, and this point is discussed in Chapter 4. Different molecules have different symmetry groups, and different symmetry groups have different irreducible representations which are given in *character tables* (see Appendix ***A***). The irreducible representation labels (called symmetry labels) are straightforward to determine and once we have labeled the energy levels in this way the molecule becomes much easier to understand. The elements of the CNPI group of a molecule all commute with the Hamiltonian of the isolated molecule in free space, and thus the CNPI group of a molecule is a symmetry group of that molecule (Chapter 7). We could use the irreducible representations of the CNPI group of a molecule to label its energy levels, but this is not always a clever thing to do. It is usually better to use a subgroup of the CNPI group called the molecular symmetry group.

The definition of the molecular symmetry (MS) group is easier to appreciate after we have considered the question "what do we do with the symmetry labels"? In general terms we use them to label energy levels that can be distinguished in the experimental results that we are interpreting, and we do not need to do more. We can say that if our symmetry group permits this then it is a sufficiently large symmetry group and it provides sufficient symmetry labeling. The molecular symmetry group, in conjunction with the spatial three-dimensional pure rotation group $\boldsymbol{K}$(spatial) [to be discussed in the next chapter], allows this. To be more specific, we use the symmetry labels to determine nuclear spin statistical weights (Chapter 8), and to identify all zero order levels that can and cannot interact as a result of considering (a) the effect of previously neglected terms in the complete Hamiltonian (Chapter 13), or (b) the effect of applying an external perturbation such as an electric or magnetic field. We also use the symmetry labels to decide which states of the molecule can be connected by transitions in the presence of electromagnetic radiation (Chapter 14). We can use the molecular symmetry group and the group $\boldsymbol{K}$(spatial) for these purposes.

3.2 THE DRAWBACKS OF USING THE CNPI GROUP

Let us consider the number of elements in the CNPI group. For a series of molecules the order of the CNPI group (twice the order of the CNP group) is as follows:

H_2	$2! \times 2 = 4$,	C_2H_6	$2! \times 6! \times 2 = 2880$,
H_2O	$2! \times 2 = 4$,	C_2H_5OH	$2! \times 6! \times 2 = 2880$,
BF_3	$3! \times 2 = 12$,	C_6H_6	$6! \times 6! \times 2 = 1036800$,
CH_3F	$3! \times 2 = 12$,	$CH_3COCH_2CH_2OH$	$4! \times 8! \times 2! \times 2 = 3870720$,
CH_4	$4! \times 2 = 48$,	$C_6H_5CH_3$	$7! \times 8! \times 2 \approx 4 \times 10^8$.
C_2H_4	$2! \times 4! \times 2 = 96$,	$(C_6H_6)(H_2O)_2$	$6! \times 10! \times 2! \times 2 \approx 10^{10}$.
SF_6	$6! \times 2 = 1440$,	C_{60}	$60! \times 2 \approx 10^{82}$.

Clearly the order of the CNPI group can be very large,[1] and it only depends on the chemical formula of the molecule; the structure of the molecule is unimportant.

As well as being very large the CNPI group almost invariably produces a symmetry classification of the levels of a molecule in which there are systematic multiple labels. The CNPI group of methane $\boldsymbol{G}_{48}$ (see Table A-29) has 10 irreducible representations and it provides a convenient example. Using $\boldsymbol{G}_{48}$ it turns out that the rotation-vibrational energy levels of a methane molecule would be labeled as being of one of the following five types: $A_1^+ \oplus A_1^-$, $A_2^+ \oplus A_2^-$,

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[1] **The exact value of 60! is given on page 15.**

$E^+ \oplus E^-$, $F_1^+ \oplus F_1^-$, or $F_2^+ \oplus F_2^-$, where the '+' and '−' superscripts are the parity labels given by the effect of the operation E^*. Such "double" labels indicate an accidental degeneracy. Such systematic degeneracies are not really accidental but we call them accidental here since they are not required by the symmetry of the CNPI group. These degeneracies, which we will now call ***structural degeneracies***, are caused by the presence of more than one ***version*** [Bone, Rowlands, Handy and Stone (1991)] of the equilibrium structure, in a given electronic state of a molecule. We will first explain what we mean by 'versions of the equilibrium structure', and then show how structural degeneracy arises.

The idea of versions of an equilibrium structure can be explained using the methane molecule as an example. In Fig. 3-1a a methane molecule is shown with the nuclei in the equilibrium configuration for the ground electronic state. If we deform the molecule through the planar configuration (Fig. 3-1b) we can invert the molecule to obtain the form shown in Fig. 3-1c. The configurations in Figs. 3-1a and 3-1c are the nuclear configurations at two identically shaped deep minima in the potential energy surface V_N [see Chapter 9] of the ground electronic state, and the configuration shown in Fig. 3-1b represents a saddle point in V_N between the minima. Figs. 3-1a and 3-1c show the two possible versions of the methane molecule in its equilibrium configuration. Different versions of the equilibrium structure arise not only in molecules, such as methane, in which they can be interchanged by inversion, but also rather commonly in molecules such as ethane (H_3CCH_3) in which they can be interchanged by torsion. There are other, less common, ways for them to arise, as we shall see when we consider the ethylene molecule. Introducing some other terminology that we will use, we can say that when a molecule ***contorts*** from one version to another it undergoes a ***degenerate rearrangement***.

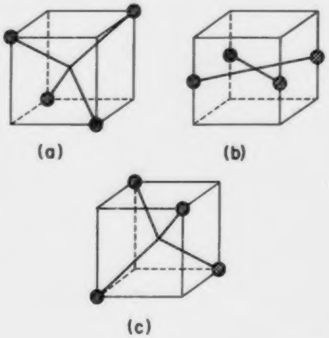

Fig. 3-1. A methane molecule in two different symmetrically equivalent equilibrium structures, (a) and (c), which can be interconverted by a deformation through the planar configuration shown in (b).

To distinguish between the different versions of the equilibrium structure of a molecule it is necessary to label the nuclei. Having labeled the nuclei of a molecule in its equilibrium structure, we determine the number of versions of the equilibrium structure by finding out how many distinct forms can be obtained by permuting the labels on identical nuclei with and without inverting the molecule. Versions are such that to interconvert them one cannot merely rotate the molecule in space but one must deform the molecule across a potential barrier.

For the methane molecule there are only two versions of the equilibrium structure as we can see once we have labeled the protons (see Fig. 3-2). We call the versions in Figs. 3-2a and 3-2b the A (for anticlockwise) version and the C (for clockwise) version, respectively, since in the A (C) version 1 → 2 → 3 is anticlockwise (clockwise) looking in the C → H_4 direction.

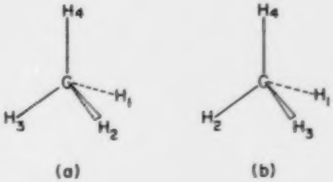

Fig. 3-2. The two versions of the equilibrium structure of a methane molecule. They are distinguishable because we have numbered the protons. The version in (a) is called the anticlockwise (A) version in the text because 1 → 2 → 3 is anticlockwise when viewed in the C → H_4 direction, and (b) is the clockwise (C) version.

The ethylene molecule was considered in Chapters 1 and 2, and it presents a further example of structural degeneracy. Labeling the protons one to four and the carbon nuclei five and six in an ethylene molecule, we see that in its electronic ground state there are altogether 12 distinct numbered versions of the equilibrium structure (shown schematically in Fig. 1-3 on page 18). To interchange pairs of these versions we either have to twist one CH_2 group relative to the other, or we have to break bonds while re-forming new ones.

To understand structural degeneracy, and how it arises when there are versions of the equilibrium structure, we need only have a qualitative appreciation of the solution of the vibrational Schrödinger equation. For the methane molecule we can choose either structure A or C in Fig. 3-2 as the equilibrium configuration for the purpose of defining the vibrational displacements. Depending upon which structure (A or C) we choose we obtain vibrational wavefunctions $\Phi_{\mathrm{A}}^{(n)}$ and energies $E_{\mathrm{A}}^{(n)}$, or $\Phi_{\mathrm{C}}^{(n)}$ and $E_{\mathrm{C}}^{(n)}$, where $n = 1, 2, 3, \ldots$, for the successive eigenstates. If, as is true in methane, the barrier in V_{N} between the minima A and C is very high then the wavefunctions $\Phi_{\mathrm{A}}^{(n)}$ are localized in the A minimum and the wavefunctions $\Phi_{\mathrm{C}}^{(n)}$ in the C minimum, with no effective penetration of either into the other minimum. In other words the molecular vibrations just occur in the region around each minimum. Since the two minima in V_{N} for methane have the same shape (they are symmetrically equivalent) the energies $E_{\mathrm{A}}^{(n)}$ and $E_{\mathrm{C}}^{(n)}$ will be identical (and identical to the observed vibrational energies $E^{(n)}$). Thus each observed vibrational energy level will be doubly degenerate, corresponding to the energies $E_{\mathrm{A}}^{(n)}$ and $E_{\mathrm{C}}^{(n)}$, and this is structural degeneracy.

If there are n versions of the global minimum (at the equilibrium structure) in the potential function V_{N} for a molecule, with no effective penetration (tunneling) of the barriers between these minima by the local wavefunctions, then each level will be n-fold structurally degenerate. When tunneling occurs the degeneracy is split, and this happens if the barrier is not high relative to the vibrational energy. In actual fact there will always be some tunneling, since potential energy barriers are not infinitely high, but often the experimental resolution is not high enough to detect the splitting. This is the case at the moment for methane. Structural degeneracy is not required by the symmetry of the CNPI group since the symmetry group is the same regardless of the height of the barrier to tunneling, and the possibility of the splitting must therefore be allowed for by the symmetry labels obtained using the CNPI group. A molecule for which no observable tunneling between minima in V_N occurs [whether these minima be symmetrically equivalent or not; see answer (vi) to Problem 3-1 on page 39] is said to be *rigid*, and one for which observable tunneling occurs is said to be *nonrigid*. It is important to realize that this definition of a rigid molecule still allows nonzero vibrational amplitudes and it allows centrifugal distortion.

No experimental splittings, torsional or otherwise, resulting from tunneling through the barriers that separate the 12 versions of ethylene (see Fig. 1-3) have been observed; the barriers in the ground electronic state potential function that separate these 12 versions are for all practical purposes insuperable and the molecule is, therefore, a rigid molecule. To determine the vibrational energy level pattern of ethylene we would only need to consider one numbered version and the shape of the one deep minimum containing that version in the potential energy surface V_N. Each of the twelve versions would have identical vibrational energy levels and these would match the observed vibrational energy levels of the molecule. Thus each of the vibrational energy levels of ethylene in its electronic ground state has a twelve-fold structural degeneracy.

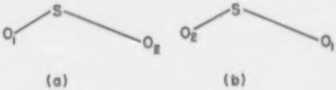

Fig. 3-3. The two versions of an unsymmetrical bent SO_2 molecule.

Structural degeneracy is present in nearly all molecules that contain identical nuclei. The lower the structural symmetry of a molecule the more versions of the equilibrium structure there will be, and the structural degeneracy increases at a dramatic rate with the size of the molecule. Simple symmetrical molecules such as SO_2 or BF_3 in their ground electronic states have no structural degeneracy since for each there is only one distinct numbered version. However, it is possible that SO_2 has unequal bond lengths at equilibrium in an excited electronic state; if true this means that in this excited electronic state there would be two distinct numbered versions of the molecule at equilibrium, as shown in Fig. 3-3, and each level would be structurally doubly degenerate if there was no tunneling between the versions. If there were an excited electronic state of BF_3 in which the molecule were planar with three unequal bond lengths at equilibrium, with no observable tunneling splittings, then each level would have a structural degeneracy of six. In methane the vibrational levels of a nonplanar electronic state with four unequal equilibrium bond lengths and no tunneling splittings, would have a structural degeneracy of 48.

We see that, although mathematically correct, the use of the CNPI group has the drawbacks of often being incredibly large and of often producing a symmetry labeling in which accidental degeneracies occur in a systematic fashion. We only need the chemical formula of a molecule in order to set up the CNPI group, and although we often know, or can guess, the equilibrium structure of a molecule and the tunneling possibilities, this information is not used in setting up the group. This information is used in setting up the molecular symmetry group, and the molecular symmetry group does not suffer from these drawbacks.

3.3 THE DEFINITION OF THE MOLECULAR SYMMETRY (MS) GROUP

To appreciate the definition of the molecular symmetry (MS) group let us consider the problem of calculating the vibrational energies of the methyl fluoride molecule. The potential energy surface V_{N} for the methyl fluoride molecule in its ground electronic state has two deep minima centered at the anticlockwise (A) and clockwise (C) labeled versions shown in Figs. 3-4a and 3-4b, respectively. To determine the vibrational energy levels a mathematician might insist that we should determine the eigenvalues of the vibrational Hamiltonian using the complete double minimum potential energy surface. However, experience tells us that there will be no observable splittings as a result of tunneling between the A and C versions for the vibrational levels that we study. Thus for all practical purposes we can determine the vibrational energy levels of the methyl fluoride molecule by solving the vibrational equation for the energy levels in one minimum, appropriate for the A version, say, with the complete neglect of the potential energy surface in the region of the other minimum. Vibrational interactions or external perturbations will only connect one A version level with another A version level in the absence of inversion tunneling. The C version will provide a duplicate set of energy levels and interactions so that the methyl fluoride molecule has twofold structural degeneracy.

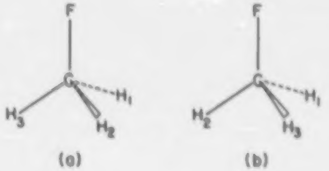

Fig. 3-4. The two versions of a methyl fluoride molecule at equilibrium where (a) is the anticlockwise (A) version and (b) is the clockwise (C) version.

We can completely understand the rotation-vibration energy levels and all possible interactions within the ground electronic state of methyl fluoride (apart from inversion tunneling) by considering only one version of the molecule. Hence we need only make a symmetry labeling of the levels of one version to obtain a sufficient symmetry labeling of the levels of the molecule. To do this we just need the CNPI group of one version of the molecule, i.e., the group

$$\{E, (123), (132), (12)^*, (23)^*, (13)^*\}; \tag{3-1}$$

this group, called $C_{3v}(M)$, was introduced in Eq. (2-13) in the answer to Problem 2-2. The $C_{3v}(M)$ group in Eq. (3-1) is the molecular symmetry group of methyl fluoride when inversion tunneling splittings are not observed. Elements in the CNPI group of methyl fluoride that interconvert the A and C versions, such as (12) or $(123)^*$, are not present in the MS group and constitute what are called [Longuet-Higgins (1963)] *unfeasible* elements of the CNPI group of methyl fluoride; we could equally well call them *useless* elements of the CNPI group. The use of the word 'unfeasible' for a permutation or permutation-inversion caused some controversy in the early days after Longuet-Higgins' paper; it seemed to suggest a 'pathway' for such an operation. Thus the alternative word 'useless' has some merit. We will, however, continue to use the word 'unfeasible' since it has become entrenched in the literature, and the false nature of the implication of a pathway is understood by those that use the groups in molecular spectroscopy.

The MS group of a molecule is obtained by deleting all elements from the CNPI group of the molecule that are unfeasible; the elements in the MS group are said to be *feasible*. An unfeasible element is one that interconverts numbered equilibrium versions of the molecule when these versions are separated by an insuperable barrier in the potential energy surface; an insuperable barrier is one that does not allow observable tunneling to occur through it on the time scale of the experiment being performed. Tunneling may not be observable if we use a low resolution experiment yet it may occur if we use a high resolution experiment. The MS group that we use to analyze the results will then be different for the two cases since the elements associated with the tunneling are feasible in the latter (high resolution) case but not in the former (low resolution) case. If splittings from inversion tunneling were observed in methyl fluoride (perhaps in highly excited vibrational states), and we wished to symmetry label the split levels, the MS group of the molecule would become equal to its CNPI group since all elements of it would be feasible. In the same way that to set up the point group for a molecule we need to know the equilibrium geometry, so to set up the MS group we need to know the equilibrium geometry and the situation with regard to vibrational tunneling.

We will use the terms 'feasible' and 'unfeasible' in two different ways. The first way is as discussed above when determining which permutations in the CNPI group should be retained in the MS group. The second way is rather closely related and it concerns the labeling of tunneling motions through barriers in the potential function of a molecule. If such tunneling motions (degenerate rearrangements) produce observable splittings or shifts then such motions will be called feasible, and if they do not produce observable splittings or shifts then they will be called unfeasible. We call geometries that are accessible along feasible tunneling paths 'accessible geometries'; thus the planar geometry of ammonia is accessible. All these definitions, of course, depend on the resolution of the experiment being used to study the molecule in question.

For the ethylene molecule the CNPI group has 96 elements and is the direct product $\boldsymbol{S}_4^{(\mathrm{H})} \otimes \boldsymbol{S}_2^{(\mathrm{C})} \otimes \mathcal{E}$ (see Problem 2-3). The CNPI group of one of the versions (a), (b), (c), or (d) shown in Fig. 1-3 can be used as the MS group of ethylene, and it consists of the eight elements given in Eq. (2-15). If we wish to use one of the numbered versions (e), (f), (g), or (h) in Fig. 1-3, in the vibrational problem, then the MS group we use is

$$\begin{aligned}&\{E, (13)(24), (12)(34)(56), (14)(23)(56),\\ &\quad E^*, (13)(24)^*, (12)(34)(56)^*, (14)(23)(56)^*\},\end{aligned} \tag{3-2}$$

whereas if we want to use one of the numbered versions (i), (j) (k) or (l) in Fig. 1-3 the appropriate MS group is

$$\begin{aligned}&\{E, (14)(23), (12)(34)(56), (13)(24)(56),\\ &\quad E^*, (14)(23)^*, (12)(34)(56)^*, (13)(24)(56)^*\}.\end{aligned} \tag{3-3}$$

To solve the vibrational problem we use one version of the ethylene molecule, and the MS group is the one appropriate for that version. Regardless of which version we chose we obtain an identical energy level pattern and symmetry labeling.

Note that for a planar molecule the inversion operation E^* is always feasible, and the MS group is the direct product of the group of feasible permutations and the inversion group $\mathcal{E} = \{E, E^*\}$.

The MS group is thus defined for a particular electronic state (and numbered version) of a molecule with regard to the experimental observation or nonobservation of tunneling splittings. It therefore uses knowledge of the molecular structure and potential energy surface to obtain a symmetry group that is much smaller than the CNPI group (in most cases), but which provides a sufficient symmetry labeling of the observed levels. We return to the methane molecule with which we began this discussion. Omitting unfeasible elements from the CNPI group $\boldsymbol{G}_{48}$ gives the molecular symmetry group $\boldsymbol{T}_\mathrm{d}(\mathrm{M})$ (see Table A-14) having five irreducible representations. Using this group the rotation-vibration levels are labeled A_1, A_2, E, F_1 or F_2 and there is no redundant double labeling as obtained using $\boldsymbol{G}_{48}$. This labeling, in combination with the labeling obtained from the group $\boldsymbol{K}$(spatial), is sufficient to understand the symmetry aspects of all intermolecular interactions and external perturbations with the exception of effects arising from inversion tunneling. If in some ultra-high resolution experiment inversion doublets were observed for methane then there would be ten rather than five distinguishable states (as far as nuclear permutation inversion symmetry were concerned) and to distinguish them one would need to use $\boldsymbol{G}_{48}$ since there would no longer be degeneracies between the states of opposite parity.

One systematic way to determine the MS group of a molecule is first to label the nuclei and then to write down the elements of the CNPI group of the molecule. The next stage is to draw all the distinct versions of the molecule at equilibrium (by permuting the labels on identical nuclei with and without inverting the molecule) and to form sets of these versions that one wishes to be connected by observable tunneling effects. To obtain the MS group it is then necessary to consider one particular set and to delete from the CNPI group of the molecule any elements that convert the versions in that set to the versions in other sets. Different sets may have different MS groups [for example, see the groups in Eqs. (2-15), (3-2), and (3-3)]. For large CNPI groups this method for determining the MS group is very clumsy, and a more efficient way is described in the Appendix of Bone, Rowlands, Handy and Stone (1991). In this approach one first writes down the versions and then determines the permutations and permutation inversions of one of the versions. By then determining the permutations that interconnect versions between which there is feasible tunneling one can rather quickly arrive at all the elements of the MS group. In the determination of larger MS groups it is useful to know that they can be written as the product of subgroups (see Section 5.7 and the Bibliographical Notes to Chapter 5).

Problem 3-1. Set up the MS groups of the following molecules in their ground electronic states: (i) CH_2F_2, (ii) HN_3, (iii) BF_3, (iv) NF_3, (v) CH_4, (vi) *trans* C(HF)CHF, and (vii) C_2H_2. Each of these molecules is such that either it does not possess more than one version of the equilibrium structure or, if it does, no observable tunneling between them occurs. Hence, they are all rigid molecules.

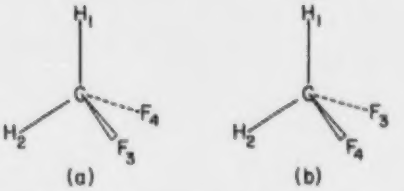

Fig. 3-5. The two versions of the equilibrium structure of a CH_2F_2 molecule.

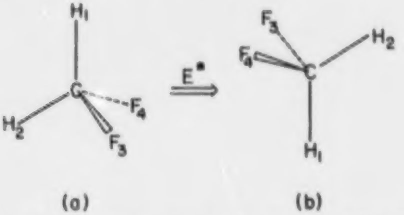

Fig. 3-6. The effect of the operation E^* on the version of CH_2F_2 given in Fig. 3-5a.

Answer. (i) CH_2F_2. We choose to label the protons 1 and 2, and the fluorine nuclei 3 and 4, so that the CNPI group is

$$\{E, (12), (34), (12)(34), E^*, (12)^*, (34)^*, (12)(34)^*\}. \qquad (3\text{-}4)$$

There are only two versions of the equilibrium structure as shown in Fig. 3-5, and no tunneling between these versions is observed. The version in Fig. 3-5a has 2-3-4 clockwise when looking in the C → H_1 direction and the version in Fig. 3-5b has them anticlockwise. The permutations (12) and (34) interconvert the versions and are thus unfeasible, whereas (12)(34) is feasible since it does not interconvert the versions. The operation E^* interconverts the versions (see Fig. 3-6 and note that the version in Fig. 3-6b is identical to the version in Fig. 3-5b; i.e., it is the anticlockwise version) so that E^* is unfeasible. The operations $(12)^*$ or $(34)^*$ do not interconvert the versions and are both feasible. The operation $(12)(34)^*$ does interconvert the versions and is unfeasible. Thus the MS group of either version of CH_2F_2 is the group

$$\{E, (12)(34), (12)^*, (34)^*\}. \tag{3-5}$$

(ii) HN_3. We choose to label the nitrogen nuclei 1, 2, and 3 so that the elements of the CNPI group are

$$\{E, (12), (23), (13), (123), (132), E^*, (12)^*, (23)^*, (13)^*, (123)^*, (132)^*\}. \tag{3-6}$$

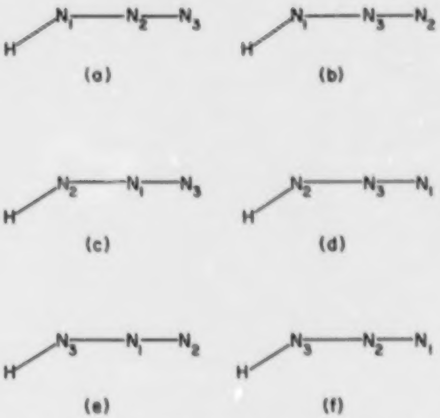

Fig. 3-7. The six versions of the equivalent equilibrium structure of an HN_3 molecule.

The versions of the equilibrium structure are shown in Fig. 3-7. There is no observable tunneling between these versions. It is easy to see that all the permutations interconvert versions. For example, we determine that the version in Fig. 3-7a is transformed as follows:

$$(12)(a) = (c), \quad (23)(a) = (b), \quad (13)(a) = (f),$$
$$(123)(a) = (d), \quad \text{and} \quad (132)(a) = (e). \tag{3-7}$$

The inversion E^* is feasible since it does not interconvert versions but all permutations accompanied by the inversion are unfeasible. Thus the MS group of

HN_3 is

$$\{E, E^*\} \tag{3-8}$$

(iii) BF_3. We label the three fluorine nuclei 1, 2, and 3 and hence the CNPI group is the same as that of HN_3 given in Eq. (3-6). However, in its equilibrium configuration BF_3 is planar with three equal BF bonds, and as a result there are no different versions of the equilibrium structure; all operations of the CNPI group are feasible. Thus the MS group of BF_3 is the same as its CNPI group and there is no structural degeneracy. The H_2O molecule is another example of a simple molecule having no structural degeneracy for which the MS group is equal to the CNPI group.

(iv) NF_3. Labeling the three fluorine nuclei 1, 2, and 3 we obtain the CNPI group of Eq. (3-6) as for HN_3 and BF_3. For this pyramidal molecule there are two versions of the equilibrium structure as shown in Fig. 3-8. To interconvert these versions we must invert the molecule, and inversion splittings are not observed. Deleting elements from the CNPI group that interconvert these versions we obtain the MS group of NF_3 as

$$\{E, (123), (132), (12)^*, (23)^*, (13)^*\}. \tag{3-9}$$

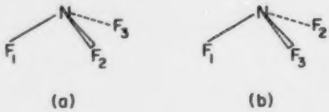

Fig. 3-8. The two versions of the equilibrium structure of an NF_3 molecule.

(v) CH_4. Labeling the four protons 1, 2, 3, and 4 we can write down the CNPI group of the molecule as the direct product of the CNP group $S_4^{(H)}$ containing $4! = 24$ elements and the inversion group $\mathcal{E}$; this has 48 elements. As discussed earlier in this chapter there are two distinct numbered versions (the A and C versions of Fig. 3-2) and inversion tunneling is not observed. Any operation, such as (12), in which one pair of protons is permuted interconverts the versions and is hence unfeasible. Any cyclic permutation of three protons is clearly feasible, and the inversion E^* is equally clearly unfeasible. From these three results we can rather quickly deduce the MS group of CH_4 by making use of the following rules:

(a) any operation that is the product of a feasible operation and an unfeasible operation is itself unfeasible, and

(b) any operation that is the product of two feasible operations is itself feasible.

For an example of the use of (a) we can look at the product

$$(123)(34) = (1234). \tag{3-10}$$

The operation (34) converts the version A to version C (since it is an unfeasible operation) and (123) then sends C to C (since it is feasible), so the product of these two operations sends A to C and is unfeasible. For methane any cyclic permutation of all four protons is unfeasible. An example of rule (b) is provided by the product

$$(123)(234) = (12)(34). \tag{3-11}$$

The operation (234) converts A to A and then (123) converts A to A, so that the product converts A to A and is feasible. We can see this latter result another way by looking at this operation as the product (12)(34), and this is the successive application of two unfeasible operations: (34)A = C, and (12)C = A, so that the product sends A to A and is feasible. We can thus appreciate a third rule:

(c) For molecules with only two distinct numbered versions the product of two unfeasible operations is itself a feasible operation. For molecules having more than two distinct numbered versions the product of two unfeasible operations may, or may not, be feasible.

For methane we deduce that all cyclic permutations of three protons and all permutations consisting of two successive pair transpositions are feasible whereas all pair transpositions, and cyclic permutations of all four protons are unfeasible. Since E^* is unfeasible we can use rules (a) and (c) to deduce that the product of a pair transposition and E^* or the product of a cyclic permutation of all four protons and E^* is feasible. The MS group of methane thus consists of the following 24 elements:

$$\begin{array}{ccccc}
E & (123) & (12)(34) & (1234)^* & (12)^* \\
 & (132) & (13)(24) & (1243)^* & (13)^* \\
 & (124) & (14)(23) & (1324)^* & (14)^* \\
 & (142) & & (1342)^* & (23)^* \\
 & (134) & & (1423)^* & (24)^* \\
 & (143) & & (1432)^* & (34)^* \\
 & (234) & & & \\
 & (243) & & &
\end{array} \tag{3-12}$$

(vi) *trans* C(HF)CHF. Numbering the protons 1 and 2, the carbon nuclei 3 and 4, and the fluorine nuclei 5 and 6, we obtain the CNPI group as the direct product

$$\{E, (12), (34), (56), (12)(34), (12)(56), (34)(56), (12)(34)(56)\} \otimes \mathcal{E}. \tag{3-13}$$

All four versions of the equilibrium structure are given in Fig. 3-9. It is important to realize that a structure such as given in Fig. 3-10 is not symmetrically equivalent to those in Fig. 3-9 since it is not obtained from any of them by relabeling identical nuclei with or without inverting the molecule. The structure in Fig. 3-10 is the *cis* structure of the molecule and is related to the *trans* structure by twisting the molecule over a potential barrier. The distinction between ***structure*** and ***version*** is discussed by Bone, Rowlands, Handy and Stone (1991). In this molecule the ground electronic state potential energy surface has four versions for the *trans* structure and four versions for the *cis* structure at a different energy from that of the *trans* structure. The shape of the potential energy surface around the *cis* and *trans* minima will be different and the vibrational energy level patterns of the *cis* and *trans* structures will be different. For *trans* $C_2H_2F_2$ the feasible elements are easy to determine and the MS group consists of

$$\{E, (12)(34)(56), E^*, (12)(34)(56)^*\}. \tag{3-14}$$

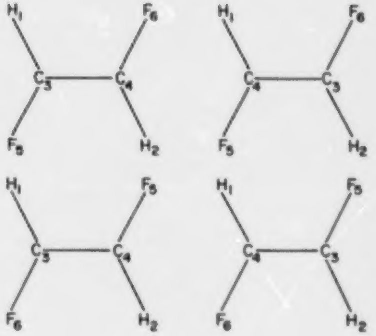

Fig. 3-9. The four versions of the equilibrium (*trans*) structure of the C(HF)CHF molecule.

The MS group of *cis* $C_2H_2F_2$ is the same as that of *trans* $C_2H_2F_2$ and if *cis-trans* tunneling occurs the MS group is still the same. The tunneling is not between versions of the equilibrium structure, so although it makes the molecule nonrigid it does not cause a splitting of any structural degeneracy and it does not enlarge the MS group.

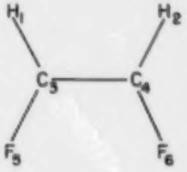

Fig. 3-10. A numbered version of the *cis* structure of the C(HF)CHF molecule.

(vii) C_2H_2. In the acetylene molecule HCCH we number the protons 1 and 2 and the carbon nuclei 3 and 4; the CNPI group is the group of eight elements given in Eq. (3-4). The operations (34), (12), $(34)^*$, and $(12)^*$ are unfeasible and the MS group is

$$\{E, (12)(34), E^*, (12)(34)^*\}. \tag{3-15}$$

For any symmetrical linear molecule the MS group consists of the four elements E, (p), E^*, and (p^*), where (p) is the simultaneous transposition of all pairs of identical nuclei symmetrically located about the molecular mid-point. For any unsymmetrical linear molecule (such as HCN) the MS group is $\{E, E^*\}$.

Problem 3-2. Set up the MS groups of the following nonrigid molecules in their ground electronic states: (i) NH_3 allowing for inversion tunneling; (ii) C_2H_4 and (iii) H_2O_2 allowing for torsional tunneling in each case.

Answer. (i) NH_3 with inversion tunneling. Numbering the protons 1, 2, and 3 the CNPI group is as for HN_3 given in Eq. (3-6), and there are two versions of the equilibrium structure as for NF_3 (see Fig. 3-8). Allowing for the effects of inversion tunneling in setting up the MS group we must include as feasible elements permutations and permutation inversions that interconvert versions across the inversion barrier. Thus the MS group of inverting NH_3 is the same as its CNPI group and this is the same as the MS group of planar BF_3.

(ii) C_2H_4 with torsional tunneling. The CNPI group of ethylene is the direct product $\boldsymbol{S}_4^{(H)} \otimes \boldsymbol{S}_2^{(C)} \otimes \mathcal{E}$ with 96 elements as discussed before. In Fig. 1-3 on page 18 the 12 versions of the equilibrium structure of an ethylene molecule in its ground electronic state are drawn schematically. Grouping these into sets within which the versions are connected by torsional tunneling we obtain the six sets [(a),(b)], [(c),(d)], [(e),(f)], [(g),(h)], [(i),(j)], and [(k),(l)] from Fig. 1-3. Let us consider the set [(a),(b)]. Examples of elements that convert the versions in this set into versions in other sets are (13), (56), (24), and (234), and these are hence unfeasible elements of the CNPI group for the set [(a),(b)]. Elements such as (12) and (34) are feasible, and combining these with the elements of the MS group of nontorsionally tunneling ethylene in the versions (a) and (b) [see Eq. (2-15)] we obtain the MS group of the torsionally tunneling versions in set [(a), (b)] of Fig. 1-3 as

$$\left\{ \begin{matrix} E & (12) & (12)(34) & (13)(24)(56) & (1324)(56) \\ & (34) & & (14)(23)(56) & (1423)(56) \end{matrix} \right\} \otimes \mathcal{E}. \tag{3-16}$$

The MS group for the set [(c), (d)] is the same as this. The MS group for the set [(e), (f)] or the set [(g), (h)] is the group

$$\left\{ \begin{matrix} E & (13) & (13)(24) & (12)(34)(56) & (1234)(56) \\ & (24) & & (14)(23)(56) & (1432)(56) \end{matrix} \right\} \otimes \mathcal{E}, \tag{3-17}$$

and the MS group for the set [(i), (j)] or the set [(k), (l)] is the group

$$\left\{ \begin{matrix} E & (14) & (14)(23) & (12)(34)(56) & (1243)(56) \\ & (23) & & (13)(24)(56) & (1342)(56) \end{matrix} \right\} \otimes \mathcal{E}. \tag{3-18}$$

Since we only consider a single set of versions of the equilibrium structure connected by allowed tunneling, and neglect the others, in a vibrational analysis, the fact that there are different MS groups poses no problems as long as we are careful to use the one appropriate to the particular set considered. These groups lead to identical energy level labelings of the appropriate sets.

(iii) H_2O_2 with torsional tunneling. The equilibrium structure of H_2O_2 in its ground electronic state is nonplanar with a dihedral angle of approximately 120°, as shown in Fig. 3-11. Labeling the protons 1 and 2, and the oxygen nuclei 3 and 4, we can label the nuclei of the configuration of Fig. 3-11 in the two ways shown in (a) and (b) of Fig. 3-12. A nonsuperposable version of the equilibrium configuration is obtained from that of Fig. 3-11 by inverting it, and the two ways of labeling this configuration are shown in (c) and (d) of Fig. 3-12. There are thus four versions of the equilibrium structure of H_2O_2 in its ground electronic state. If there were no observable tunneling between these structures each vibrational level would have a fourfold structural degeneracy and the MS group would be

$$\{E, (12)(34)\}. \tag{3-19}$$

Allowing for torsional tunneling the interconversions (a) ↔ (c) and (b) ↔ (d) of Fig. 3-12 are feasible, and we have two sets of structures, [(a),(c)] and [(b), (d)]. The MS group for either of these sets is

$$\{E, (12)(34), E^*, (12)(34)^*\}. \tag{3-20}$$

In H_2O_2 torsional tunneling is observed and the MS group is as given in Eq. (3-20).

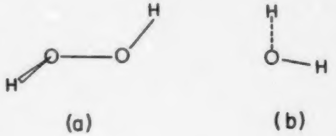

Fig. 3-11. The H_2O_2 molecule in its equilibrium configuration; (a) is a view from the side and (b) is an end on view.

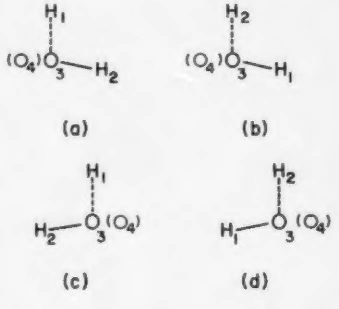

Fig. 3-12. The four versions of the equilibrium structure of an H_2O_2 molecule shown viewed end on. The oxygen atom O_4 is behind the oxygen atom O_3 in the four figures.

The H_2S_2 molecule has a similar equilibrium structure to that of H_2O_2, with a dihedral angle of about 90°. Except in ultrahigh resolution Lamb-dip experiments [Mittler, Yamada and Winnewisser (1990) and references therein] H_2S_2 has no observable torsional tunneling in its ground state, and thus for normal spectroscopic work on this state its MS group is as given in Eq. (3-19); no permutation inversion elements are present. A molecule having no permutation inversion elements in its MS group has optically active versions and H_2S_2 is a simple example of this.

3.4 WEAKLY BOUND CLUSTER MOLECULES

Beginning with the pioneering work of Harry Welsh and his colleagues at the University of Toronto in the 60's and early 70's [Watanabe and Welsh (1964), Kudian, Welsh and Watanabe (1965), Kudian and Welsh (1971), and McKellar and Welsh (1971,1972)] the high resolution spectroscopic study of weakly bound molecular clusters, often called van der Waals molecules, has grown into a topic of widespread interest and importance. We define a weakly bound molecular cluster as a complex formed in the gas phase (or in a molecular beam) between two or more stable neutral monomers; the monomers can be atoms or molecules. We will call the monomer units within the cluster *moieties* so that we are free to use the word molecule for the cluster itself without ambiguity. By far the most widely studied molecules of this type are dimers: there are homogeneous dimers (having identical moieties) such as $(H_2)_2$, $(HF)_2$, $(H_2O)_2$, and $(NH_3)_2$, and heterogeneous dimers (having dissimilar moieties) such as $Ar-H_2$, $Ar-HCl$, $OCO-HF$, and $C_6H_6-H_2O$. Larger clusters are also the subject of many investigations, and systems such as Ar_n, Na_n, $(H_2O)_n$, $NaCl(H_2O)_n$ and $C_6H_6(H_2O)_n$ are of special importance.

These molecules are not well described as having an equilibrium structure about which small amplitude vibrations occur, although they obviously do have an equilibrium structure (and usually many versions of it). In the equilibrium structure the bonds (called 'van der Waals' bonds) connecting the atoms of different moieties are much longer than a covalent electron pair chemical bond, and they have relatively low dissociation energies and weak angular rigidity. As a result torsional motions about them, large scale bending of one or more of them, and even the concerted breaking with the forming of new van der Waals bonds can occur. An example of the latter occurs in the feasible tunneling of the HF dimer between the versions $H_1F_2-H_3F_4$ and $F_2H_1-F_4H_3$, where the F_2-H_3 bond breaks as the new H_1-F_4 bond forms; this motion was discovered by Dyke, Howard and Klemperer (1972). As a result of these feasible tunneling motions weakly bound molecular clusters are usually extremely nonrigid, and provide systems for which the molecular symmetry group has achieved widespread application.

The molecular symmetry group of a weakly bound cluster molecule could be set up in the general manner described above for any molecule (rigid or nonrigid) by identifying the feasible elements of the CNPI group. However, for these systems as the number of moieties increases the CNPI group can become truly gigantic. Even more disconcerting is the fact that the potential energy surface of such clusters can have a huge number of minima (not necessarily all symmetrically equivalent) with a large number and variety of saddle points connecting them. Finding the equilibrium structure and determining the feasible degenerate rearrangements can be a difficult task. The determination of the MS groups of such molecules thus becomes a special case. Some modeling of the topology of the potential energy surface using theoretical calculations is virtually a prerequisite for all but the simplest systems in order that one can gain insight into the equilibrium structure, the possible tunneling pathways and the relevant tunneling splittings. Minima other than those at the global minimum of the potential function (i.e., other than at versions of the equilibrium structure) may also be important for the analysis of the spectrum.

For a weakly bound cluster molecule it is frequently necessary to consider the subgroup of the CNPI group obtained by deleting only elements that involve unfeasible contortions of each of the moieties; we call this group the full cluster tunneling (FCT) group. This group is obtained from the CNPI group of the molecule by deleting all elements that correspond to degenerate rearrangements involving a path identical to one that would be unfeasible in an isolated moiety. Thus in the methane-argon dimer the FCT group would be the same as the MS group of the methane moiety and E^* would be unfeasible; this group happens to be the MS group of the dimer. However, sometimes the MS group of the cluster molecule is a subgroup of the FCT group.

The first example of a weakly bound cluster molecule that we consider is the hydrogen dimer[2] $(H_2)_2$. We label the protons $H_1H_2{-}H_3H_4$. This is an example of a dimer in which the van der Waals bond (which we can draw for this molecule as connecting the mid-points of the moieties) is only weakly anisotropic so that all angular orientations of each moiety with respect to the bond are feasible. Thus all elements of the CNPI group are feasible except those such as (13) that involve the breaking and re-forming of the covalent H–H bonds of the moieties, and the MS group is the FCT group; this is given by

$$\left\{ \begin{matrix} E & (12) & (12)(34) & (13)(24) & (1324) \\ & (34) & & (14)(23) & (1423) \end{matrix} \right\} \otimes \mathcal{E}. \tag{3-21}$$

For the isotopomer $(HD)_2$ we label the nuclei $H_1D_2{-}H_3D_4$. Since H and D nuclei are not identical the permutations (12) and (34) cannot be present in the symmetry group and so the MS group is

$$\{E, (13)(24), E^*, (13)(24)^*\}. \tag{3-22}$$

Such a weakly anisotropic intermoiety bond as is present in the hydrogen dimer usually only occurs for bonds to rare gas or H_2 moieties. A more typical example is the HF dimer already mentioned above. For the HF dimer the two versions of the equilibrium structure are approximately as shown in Figs. 3-13a and 3-13c, and the structure at the saddle point transition state between them is as shown in Fig. 3-13b. The tunneling motion between these versions involves the breaking and forming of a van der Waals bond at the transition state. Dyke, Howard and Klemperer (1972) discovered that this tunneling is feasible (producing a splitting of 0.65 cm^{-1}) in a very important microwave spectroscopy study, and this means that the MS group is the FCT group given in Eq. (3-22) above (when we number the nuclei $H_1F_2{-}H_3F_4$).

The water dimer [Dyke and Muenter (1974), Dyke (1977), Dyke, Mack and Muenter (1977)] is an example with more than one feasible degenerate rearrangement path. Numbering the protons 1 and 2, and the oxygen nucleus 5,

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[2] This dimer is discussed at greater length in Section 16.5.1.

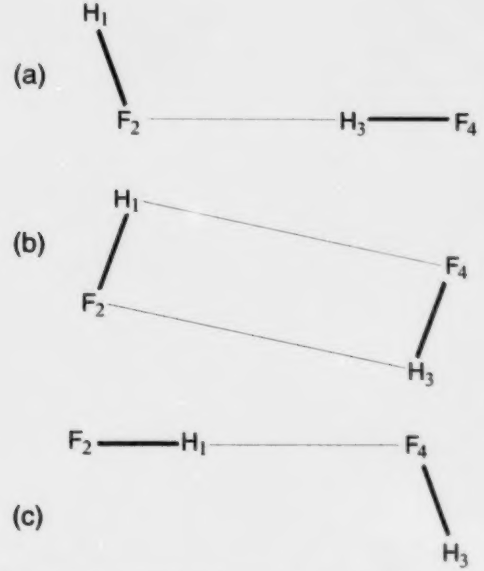

Fig. 3-13. An HF dimer molecule in its two different versions of the equilibrium structure, (a) and (c), which can be interconverted by a tunneling through the symmetrical transition state shown in (b).

on one water moiety, and the protons 3 and 4, and the oxygen nucleus 6, on the other, then the FCT group is essentially the same as that for the hydrogen dimer:

$$\left\{ \begin{array}{lllll} E & (12) & (12)(34) & (13)(24)(56) & (1324)(56) \\ & (34) & & (14)(23)(56) & (1423)(56) \end{array} \right\} \otimes \mathcal{E}. \tag{3-23}$$

This group is the same as the MS group $\boldsymbol{G}_{16}$ of ethylene. If tunnelings between all versions of the equilibrium structure (except those involving the breaking of the covalent OH bonds in the moieties) are feasible then this is the MS group. However, to see if this is the case, and to use the group, we need to study the situation further with the help of a theoretical study of the effects of the various tunneling processes [Coudert and Hougen (1988,1990)] and some *ab initio* calculations [Smith, Swanton, Pople, Schaefer and Radom (1990)]. The shape of the equilibrium structure is determined to be as shown approximately in Fig. 3-14; this is very much like the HF dimer in that there is a hydrogen bond between the moieties with one moiety being the hydrogen bond donor (one of its protons forms the hydrogen bond) and the other moiety being the hydrogen bond acceptor.

By studying Fig. 3-14 we determine that there are eight versions of the equilibrium structure (ignoring the possibility of breaking the covalent OH bonds in the moieties): each of the four protons in turn can be the hydrogen

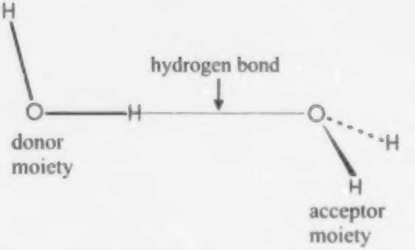

Fig. 3-14. The equilibrium structure of the water dimer

bonding proton, and for each of these four choices there are two choices for the labeling of the protons in the acceptor moiety.[3] The eight versions of the equilibrium structure are shown in Fig. 3-15, and we label these versions (1) to (8) as in Fig. 4 of Coudert, Lovas, Suenram and Hougen (1987).

We have not drawn all these versions the same way around in order that the degenerate rearrangements that closely parallel the one occurring in the HF dimer should be apparent. The four solid double headed arrows [such as that which connects (1) and (4)] show the degenerate rearrangement with the lowest hindering barrier, and this is essentially a rotation of the acceptor moiety about its two-fold axis. This has a barrier of about 200 cm^{-1}, and is called the *acceptor-tunneling* path. The eight dashed double headed arrows [such as that which connects (1) and (5)] show the degenerate rearrangement that parallels that in the HF dimer. In this rearrangement the acceptor moiety rotates into the hydrogen bond while, in a geared fashion, the donor moiety rotates out. This has a barrier of about 300 cm^{-1}, and is called the ***donor-acceptor interchange*** path. The four broad double headed arrows [such as that which connects (1) with (2)] shows the degenerate rearrangement that involves the concerted rotation of the donor moiety (to exchange which of its protons participates in the hydrogen bond) and inversion at the O atom of the acceptor moiety. This has a barrier of about 650 cm^{-1}, and is called the *donor-tunneling* or *bifurcation* path. We could imagine different situations depending on the feasibility or not of the various degenerate rearrangements, and depending on the experimental resolution with which the rotation-vibration energy levels were measured. If all degenerate rearrangements were unfeasible the water dimer would be a rigid molecule and the MS group of versions (1) to (4) would be

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[3] If there were no plane of symmetry in the equilibrium structure (achieved if the structure at equilibrium were obtained by rotating the acceptor moiety slightly about the hydrogen bond in Fig. 3-14) there would be 16 versions. This is in keeping with the general remark made on page 32 that the number of versions of the equilibrium structure goes up as the symmetry of the equilibrium structure goes down.

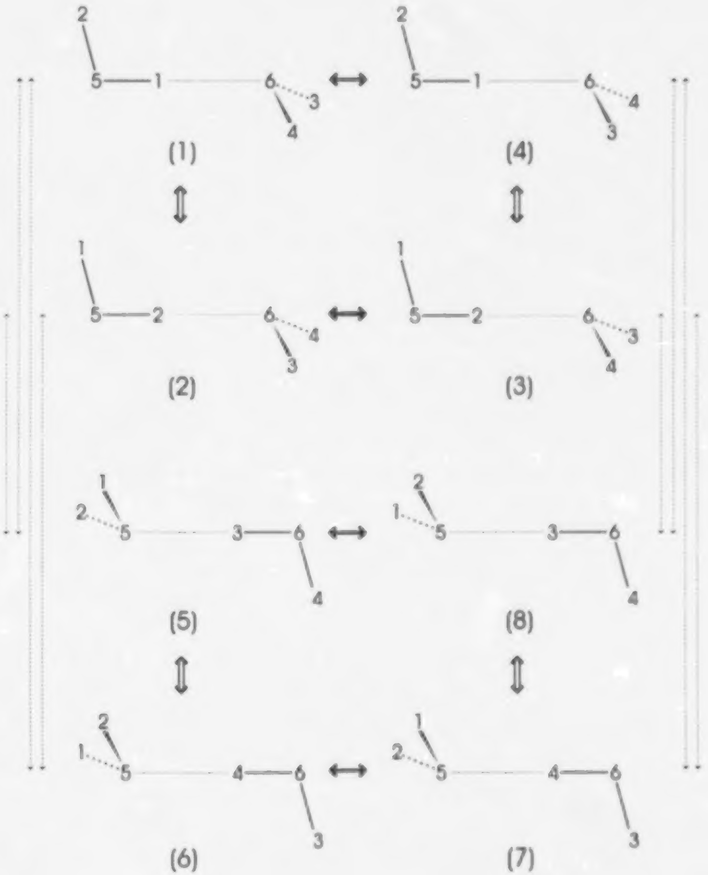

Fig. 3-15. The eight different versions of the equilibrium structure of a water dimer molecule, (1) through (8), which can be interconverted by the various tunneling rearrangements indicated by the double headed arrows.

$\{E,(34)^*\}$, whereas that of versions (5) to (8) would be $\{E,(12)^*\}$. Each of the eight versions would have the same rotation-vibration energy levels. Ignoring the structural degeneracy resulting from bond breaking in the moieties each level would have an eight-fold structural degeneracy. If the acceptor-tunneling path (solid arrows) were considered feasible but the other degenerate rearrangements still unfeasible then (34) would become feasible for versions (1) through (4), and (12) would become feasible for versions (5) through (8). The MS group of versions [(1),(4)] and [(2),(3)] would become $\{E,(34),E^*,(34)^*\}$ and the MS group of versions [(5),(8)] and [(6),(7)] would become $\{E,(12),E^*,(12)^*\}$. The molecular energy levels would now have a resolved splitting into two levels each of which would have a four-fold structural degeneracy remaining because of the unfeasibility of the other degenerate rearrangements. If the donor-acceptor interchange path were also considered to be feasible then all eight minima would be accessible to each other and in this circumstance the MS group would be the FCT group given in Eq. (3-23). No further splittings would be possible although the tunnelings caused by other paths [such as the donor-tunneling path] would modify the splittings caused by the acceptor-tunneling and donor-acceptor interchange paths just considered. The experimental situation in this molecule is that with the normal resolution of microwave spectroscopy all these possible splittings are resolved and the MS group that one needs to label the distinguishable energy levels is the FCT group given in Eq. (3-23).

Although in the light of the experimental observations and the *ab initio* calculations it is not the case, it would be instructive for the reader to determine the MS group in the event that the donor-tunneling and acceptor-tunneling paths were feasible but the donor-acceptor interchange were not. Permutations that interchange the moieties would not be feasible in this case.

As an example of a dimer having a rather large number of versions of its equilibrium structure, and also having more than one degenerate rearrangement path, we consider the benzene-water dimer. We base this discussion on the theoretical calculations of Gregory and Clary (1996). We label the pairs of bonded CH nuclei of the benzene moiety 1, 2, ..., 6 cyclically, and the protons on the water moiety 7 and 8. The equilibrium structure of the dimer can be approximately described as having one OH bond of the water moiety perpendicular to the plane of the benzene moiety with the H atom of that bond pointing at the center of the ring; the benzene ring acting as a hydrogen bond acceptor (see Fig. 3-16; H_8, which forms the hydrogen bond is below the oxygen atom in this figure). There are 24 versions of the equilibrium structure of this molecule.

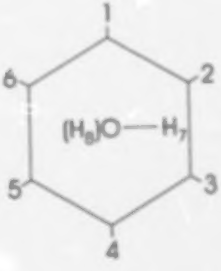

Fig. 3-16. A version of the equilibrium structure of the benzene-water dimer.

For the benzene-water dimer the internal rotation about the hydrogen bond has a very low six-fold barrier, and thus this internal rotation tunneling will produce a large splitting; this means that permutations such as (123456), (135)(246) and (14)(25)(36) are feasible. This rearrangement connects six versions of the equilibrium structure, and there are four distinct sets of six such versions depending on which H forms the hydrogen bond, and on which face of the benzene molecule accepts this hydrogen bond. There is an intermediate barrier to the tunneling motion that involves the exchange of the water moiety hydrogen bonds; in this motion there is a rotation of the H_2O so that the hydrogen atoms involved in the hydrogen bond are exchanged. Considering this motion to be feasible means that the permutation (78) is feasible. A third degenerate rearrangement that is possible on this surface is the reverse ring tunneling that involves a concerted rotation of both moieties so that the other face of the benzene ring is involved in the hydrogen bond. This motion is hindered by a high barrier and can be considered unfeasible. Thus permutations such as (12)(36)(45) and (15)(24), and the inversion E^*, are unfeasible. In this circumstance the 24 versions of the equilibrium configuration divide into two distinct sets of 12; within each set of 12 tunneling is feasible, but tunneling is unfeasible between the minima of the two sets. With these considerations the MS group of the benzene-water dimer is of order 24. This group, $\boldsymbol{G}_{24}$, is the direct product of the group $\boldsymbol{C}_{6v}(\mathrm{M})$ with elements

$$\left\{ \begin{array}{cccccc} E & (123456) & (135)(246) & (14)(25)(36) & (26)(35)^* & (14)(23)(56)^* \\ & (165432) & (153)(264) & & (31)(46)^* & (25)(34)(61)^* \\ & & & & (42)(51)^* & (36)(45)(12)^* \end{array} \right\}. \tag{3-24}$$

and the group

$$\{E, (78)\}. \tag{3-25}$$

$\boldsymbol{G}_{24}$ is half the size of the FCT group which would be given by the direct product $\boldsymbol{G}_{24} \otimes \mathcal{E}$. The FCT group would be the MS group if the reverse ring tunneling were also feasible. If we chose to consider the hydrogen exchange tunneling and the reverse ring tunneling as both being unfeasible then the MS group would simply be the group $\boldsymbol{C}_{6v}(\mathrm{M})$ given in Eq. (3-24). This is the MS group of the benzene-argon dimer [see van der Avoird (1993)]. If there were no feasible degenerate rearrangements, i.e., if the molecule were rigid, then the MS group of the version of the benzene-water cluster molecule given in Fig. 3-16 would be the $\boldsymbol{C}_s(\mathrm{M})$ group

$$\{E, (14)(23)(56)^*\}. \tag{3-26}$$

In the Bibliographical Notes of Chapter 16 we list several recent review articles that cover various aspects of the study of weakly bound cluster molecules.

3.5 THE MS GROUP FOR LEVELS OF MORE THAN ONE ELECTRONIC STATE

So far in this chapter we have set up the MS group in order to classify the rotation-vibration levels of a single electronic state[4] of a molecule. The electronic wavefunctions of a molecule depend on the nuclear coordinates, and for a particular electronic state, we can classify the electronic wavefunction, and hence rovibronic wavefunctions, in the MS group of that electronic state. It is sometimes necessary to consider rovibronic levels of more than one electronic state in a given problem; for example, we might want to consider interactions between rovibronic levels belonging to different electronic states or to consider electric dipole transitions between electronic states. In these circumstances we must generalize our definition of the MS group so that it will be appropriate for classifying simultaneously the rovibronic levels of more than one electronic state.

Clearly, just as for the purposes of classifying the levels of a single electronic state, we could use the CNPI group for classifying the levels of all electronic states of a molecule. However, we wish to use the smallest group necessary for a sufficient symmetry labeling of the levels, and this group is the MS group. The definition of the MS group given earlier for one electronic state can be applied when we wish to study simultaneously more than one electronic state by generalizing the concept of feasibility. The generalization is to say that an unfeasible element of the CNPI group interconverts versions of the equilibrium structure of one of the electronic states being considered when these structures are separated by an insuperable potential energy barrier and when they cannot be interconverted by transitions to and from any of the other electronic states being considered.

An example of the application of this extended definition is to the determination of the MS group appropriate in the study of the $V \leftarrow N$ electronic transition in ethylene [see Merer and Watson (1973), and Watson, Siebrand, Pawlikowski and Zgierski (1996)]. The ethylene molecule is planar in the equilibrium structure of the N ground electronic state, as we have discussed above, but in the V excited electronic state it is nonplanar at equilibrium with one CH_2 twisted at 90° relative to the other about the C-C bond. The MS group of the numbered ground state version in Fig. 1-3a is given in Eq. (2-15). Within the ground state this numbered version has negligible tunneling into the other numbered versions. However, by transitions to and from the V state the version in Fig. 1-3a can be converted into the version in Fig. 1-3b. Thus the elements (12) and (34) are feasible here and are in the MS group for use in simultaneously classifying the levels of the N and V electronic states of ethylene: these elements are unfeasible for either of the electronic states taken by themselves. Hence the MS group for use in simultaneously classifying the levels of the N and V states is the group given in Eq. (3-16). The excited R electronic state of ethylene is nonplanar and in a study of the $R \leftarrow X$ band system the same

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[4] See Chapter 9 for a discussion of electronic states.

MS group is required [see Merer and Schoonveld (1969)]. The symmetry of ethylene, and the use of that symmetry in understanding the *V*-*N* resonant Raman spectrum, is discussed in Section 15.4.6.

3.6 SUMMARY

The CNPI group of a molecule can be used to label its energy states with irreducible representation labels. However, for a molecule in an electronic state in which there are two or more versions of the equilibrium structure, between which tunneling produces no observable splittings, this classification scheme is more detailed than necessary. To symmetry label the energy levels as much as is necessary, that is in order to distinguish between energy levels that are distinguishable experimentally, it is sufficient to use a particular subgroup of the CNPI group. This subgroup, called the molecular symmetry (MS) group, is obtained from the CNPI group by deleting all unfeasible elements. If we are only interested in considering a single electronic state of a molecule then an unfeasible element is one that interconverts versions of the equilibrium structure that are separated by an insuperable barrier in the potential energy function (on the time scale of the experiment); feasible elements maintain an equilibrium version as itself or interconvert versions between which tunneling (such as by torsion or inversion) produces observable splittings. Rigid molecules are defined to be molecules for which all such tunneling rearrangements are unfeasible; nonrigid molecules have at least one feasible tunneling rearrangement. Weakly bound cluster molecules (often called van der Waals molecules) form a special class, and such molecules are treated separately. If we are interested in considering two or more electronic states of a molecule at once, because we wish to study interactions or transitions between them, then the definition of a feasible element must be extended to include elements that connect versions that can be interconverted by transitions to and from any of the other electronic states being considered.

BIBLIOGRAPHICAL NOTES

Bone, Rowlands, Handy and Stone (1991). It is shown how the MS group can be used to determine the transition state for an intramolecular rearrangement, and that the level of symmetry of the transition state is governed by very simple rules. The analysis is applied to the acetylene trimer in which there are two transition state structures that together allow full interconversion between the 16 versions of the global minimum.

Quack (1977). Molecular symmetry group ideas are used to relate the symmetries of the rovibronic states of product and reagent molecules in a chemical reaction.

4

Rotation Groups and Point Groups

The MS group of a molecule is a symmetry group because the molecular energy is invariant to its elements. Macroscopic objects have symmetry because of their geometrical shape, and this type of symmetry is based on entirely different principles from that of energy invariance. This type of symmetry is also used to set up symmetry groups of molecules; these groups are called rotation groups and point groups. The way one applies these geometrical symmetry groups to molecules is explained, and the relationship between them and the MS group is discussed.

4.1 ROTATIONAL SYMMETRY AND THE ROTATION GROUP

In Fig. 4-1a we show an equilateral triangular prism, and in Fig. 4-1b a box, the "prism box," into which the prism exactly fits when the lid is closed. There are six ways in which the prism can be placed to fit into the prism box depending on which of the two triangular faces is down and on which of the three triangle vertices is in a given corner of the box; there are thus six equivalent spatial orientations of an equilateral triangular prism. Similarly a solid cube can be placed inside a "cube box" that exactly fits it in any one of 24 different ways. The number of different ways that a solid body can be placed into a box that exactly fits it is a measure of the rotational symmetry of the object, and a cube has more rotational symmetry than an equilateral triangular prism.

To be more specific about the rotational symmetry of an object we introduce ***rotational symmetry axes*** and ***rotational symmetry operations***. As drawn in Fig. 4-1 the equilateral prism can be dropped straight into the prism box. If the prism is rotated by $2\pi/3$ or $4\pi/3$ radians about an axis passing vertically through the center of the triangular faces it can again be dropped straight into the prism box; such an axis is termed a rotational symmetry axis, and the rotations through $2\pi/3$ or $4\pi/3$ radians about the axis are rotational symmetry operations. A rotational symmetry operation of a solid object is a rotation of the object, about an axis passing through its center of mass, that leaves the object in an equivalent spatial orientation; the axis about which the rotation

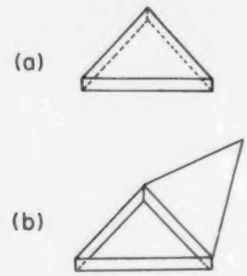


Fig. 4-1. (a) An equilateral triangular prism and (b) the "prism box" into which it exactly fits when the lid is closed.

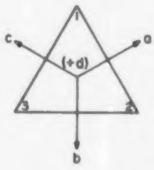
takes place is called a rotational symmetry axis. To specify the rotational symmetry axes of the prism we label the vertices and introduce a, b, c, and d axes as shown in Fig. 4-2. Each of the a, b, c, and d axes is a rotational symmetry axis and the rotational symmetry operations are

C_{2a}	a rotation through π radians about the a axis,
C_{2b}	a rotation through π radians about the b axis,
C_{2c}	a rotation through π radians about the c axis,
C_{3d}	a rotation through $2\pi/3$ radians in a right handed sense about the d axis (this takes vertex 1 to where vertex 3 was), and
C_{3d}^2	a rotation through $4\pi/3$ radians in a right handed sense about the d axis.

Including the identity operation E (that of doing no rotation) with these five operations, and defining multiplication of these operations to be their successive application, we obtain the rotational symmetry group [or *rotation group*] $\boldsymbol{D}_3$:

$$\boldsymbol{D}_3 = \{E, C_{2a}, C_{2b}, C_{2c}, C_{3d}, C_{3d}^2\}. \tag{4-1}$$

Fig. 4-2. The axis and vertex labeling convention used for an equilateral triangular prism. The $(+d)$ indicates that the d axis is pointing up out of the page.



$\boldsymbol{D}_3$ is the rotational symmetry group of an equilateral triangular prism. The multiplication table[1] for the elements of $\boldsymbol{D}_3$ is given in Table 4-1. The reader is urged to check that this table is correct, and to use it to prove that $\boldsymbol{D}_3$ is a group by testing that the four group axioms (given on page 14) are obeyed. As an example of an entry in the table we show, in Fig. 4-3, that

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[1] We define the axes to move with the prism (i.e., 'body-fixed') when it is rotated. If the axes remain fixed in space the multiplication table will be different; see Eq. (10-94).

$$C_{3d}^2 C_{2a} = C_{2b}. \tag{4-2}$$

The application of each of the six operations of the $\boldsymbol{D}_3$ group to the equilateral triangular prism produces the six different ways that the prism can be placed into the prism box. The operations C_{2a}, C_{2b}, and C_{2c} are *twofold rotation operations*, since if done twice they are equivalent to E, and the operation C_{3d} is a threefold rotation operation. The *a*, *b*, and *c* axes are called twofold rotation axes and the *d* axis is a threefold rotation axis; rotation axes must pass through the center of mass of the object. An equilateral triangular prism is said to ***have*** $\boldsymbol{D}_3$ rotational symmetry or to ***belong*** to the $\boldsymbol{D}_3$ rotational symmetry group.

Table 4-1

The multiplication table of the rotation group $\boldsymbol{D}_3$[a]

	E	C_{2a}	C_{2b}	C_{2c}	C_{3d}	C_{3d}^2
E:	E	C_{2a}	C_{2b}	C_{2c}	C_{3d}	C_{3d}^2
C_{2a}:	C_{2a}	E	C_{3d}	C_{3d}^2	C_{2b}	C_{2c}
C_{2b}:	C_{2b}	C_{3d}^2	E	C_{3d}	C_{2c}	C_{2a}
C_{2c}:	C_{2c}	C_{3d}	C_{3d}^2	E	C_{2a}	C_{2b}
C_{3d}:	C_{3d}	C_{2c}	C_{2a}	C_{2b}	C_{3d}^2	E
C_{3d}^2:	C_{3d}^2	C_{2b}	C_{2c}	C_{2a}	E	C_{3d}

[a] Each entry represents the result of first applying the operation at the top of the column and then applying the operation at the left end of the row. The axes are body-fixed.

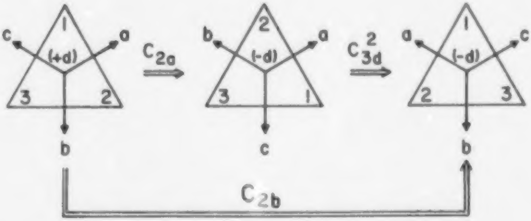

Fig. 4-3. Diagram to show that $C_{3d}^2 C_{2a} = C_{2b}$ in the $\boldsymbol{D}_3$ rotation group of Eq. (4-1). The $(-d)$ indicates that the d axis is pointing down into the page. The axes are body-fixed.

The rotational symmetry of an object is obtained by determining the number and type of rotational symmetry axes that are present. An object having one *n*-fold rotational symmetry axis, and no other rotational symmetry axes, has $\boldsymbol{C}_n$

rotational symmetry. For example, a square based pyramid has $\boldsymbol{C}_4$ rotational symmetry and the $\boldsymbol{C}_4$ rotation group has elements $\{E, C_4, C_4{}^2, C_4{}^3\}$, where the rotations are about the vertical axis of the pyramid. An object having one n-fold rotation axis, and n twofold rotation axes perpendicular to it, has $\boldsymbol{D}_n$ rotational symmetry. The rotation group of a regular tetrahedron has order 12 and is called $\boldsymbol{T}$, and that of a cube has order 24 and is called $\boldsymbol{O}$.

The rotation group of a sphere consists of all rotations about any axis that passes through the center of mass of the sphere. We can specify a given rotation operation by specifying the direction of the axis of rotation relative to the space fixed axis system, for which we need two angles (α and β, say), and by specifying the amount of the rotation about this axis, for which we need another angle (γ, say). To each rotation there corresponds a set of values of these parameters, where we have the restrictions (required so that we only go over space once)

$$0 \le \alpha \le 2\pi, \qquad 0 \le \beta \le \pi, \qquad 0 \le \gamma \le 2\pi. \tag{4-3}$$

This group is called the ***three-dimensional pure rotation group K***, and it has an infinite number of elements, i.e., it is an ***infinite group***. An infinite group whose elements are specified by continuously variable parameters, as is the case here (the parameters being α, β, and γ) is said to be a ***continuous group***. Two other continuous rotation groups are the $\boldsymbol{C}_\infty$ and $\boldsymbol{D}_\infty$ groups. The $\boldsymbol{C}_\infty$ group is the rotation group of a cone and the $\boldsymbol{D}_\infty$ group is the rotation group of a cylinder.

4.2 THE ROTATION GROUP SYMMETRY OF MOLECULES

In the application of rotation groups to molecules only three rotation groups are used: $\boldsymbol{D}_2$, $\boldsymbol{D}_\infty$, and $\boldsymbol{K}$. The group $\boldsymbol{K}$ is used in two ways: either as ***the molecular three-dimensional pure rotation group***, which we denote $\boldsymbol{K}$(mol), or as ***the spatial three-dimensional pure rotation group*** $\boldsymbol{K}$(spatial). The group $\boldsymbol{K}$(mol) consists of all rotations of a molecule about all axes passing through the molecular center of mass and fixed to the molecule, and the group $\boldsymbol{K}$(spatial) consists of all rotations of a molecule about all axes passing through the molecular center of mass and fixed in space. These two groups are different and are used in different ways.

The energy of any isolated molecule in free space (where there are no external electric or magnetic fields) is not altered by rotating all the electrons and nuclei in the molecule about an axis fixed in space that passes through the center of mass of the molecule; the energy of an isolated molecule is therefore invariant to all the operations of the group $\boldsymbol{K}$(spatial). Using the definition of a "symmetry group" to mean a group of elements that do not change the energy of a molecule (just as we do when we call the CNPI group or the MS group a symmetry group), the group $\boldsymbol{K}$(spatial) is a symmetry group for any isolated molecule in field free space. The use of this group is the basis for our labeling of molecular energy levels with angular momentum quantum numbers, and this is looked into further in Section 7.3.2. As far as rotation groups consisting of rotation operations about molecule fixed axes (which we call *molecular rotation groups*) are concerned we use the group $\boldsymbol{K}$(mol) for classifying the rotational states of spherical top molecules (such as methane), the group $\boldsymbol{D}_\infty$ for classifying the rotational states of symmetric top molecules (such as methyl fluoride), and the group $\boldsymbol{D}_2$ (sometimes called $\boldsymbol{V}$) for classifying the rotational states of all other molecules (asymmetric top molecules such as water). The use of these groups will be discussed in Section 12.6.

4.3 REFLECTION SYMMETRY AND THE POINT GROUP

In Fig. 4-4 a pyramid with an equilateral triangular base is drawn; this three-dimensional figure will be used to introduce the concept of a point group. The pyramid has threefold rotational symmetry about the *d* axis, and it also has *reflection symmetry* in the *ad, bd,* and *cd* planes. A reflection symmetry operation for a three-dimensional object is a reflection of the object through a plane (a reflection symmetry plane) that leaves the object in an equivalent spatial orientation; the plane will pass through the center of mass of the object and this center point will be common to all rotational symmetry axes and reflection symmetry planes (hence the name *point* group). The point group of a three-dimensional object consists of all rotation symmetry operations, all reflection symmetry operations, and of all possible products of such operations (although the individual rotation and reflection operations that make up a rotation-reflection product symmetry operation do not necessarily have to be symmetry operations). The point group of the pyramid in Fig. 4-4 is called $\boldsymbol{C}_{3\mathrm{v}}$, and it consists of the rotation operations E, C_{3d}, and C_{3d}^2, plus the operations of reflection in the planes *ad, bd,* and *cd*; we will call these reflection symmetry operations σ_{ad}, σ_{bd}, and σ_{cd}. The operations E, C_{3d}, and C_{3d}^2 form the rotational subgroup of $\boldsymbol{C}_{3\mathrm{v}}$; the rotational subgroup of the point group of an object consists of E and of all the rotational symmetry operations in the group (it is the rotational symmetry group of the object).

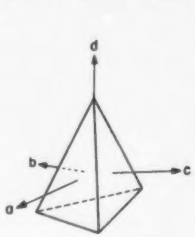

Fig. 4-4. An equilateral triangular based pyramid with the axes used in describing its symmetry.

In naming the point groups we use the *Schönflies notation*, and the possible names in this notation are:

$$\boldsymbol{C}_s(=\boldsymbol{C}_{1\mathrm{v}}=\boldsymbol{C}_{1\mathrm{h}}=\boldsymbol{S}_1),\ \boldsymbol{C}_i(=\boldsymbol{S}_2),\ \boldsymbol{C}_n,\ \boldsymbol{D}_n,\ \boldsymbol{C}_{n\mathrm{v}},\ \boldsymbol{C}_{n\mathrm{h}}(=\boldsymbol{S}_n \text{ with } n \text{ odd}),$$
$$\boldsymbol{D}_{n\mathrm{d}},\ \boldsymbol{D}_{n\mathrm{h}},\ \boldsymbol{S}_n(n \text{ even}),\ \boldsymbol{T},\ \boldsymbol{T}_\mathrm{d},\ \boldsymbol{O},\ \boldsymbol{O}_\mathrm{h},\ \boldsymbol{I},\ \boldsymbol{I}_\mathrm{h},\ \text{and } \boldsymbol{K}_\mathrm{h},$$

where n is an integer (for continuous point groups it is infinity). Each of these point groups consists of a certain definite set of symmetry operations (rotations, reflections, and rotation-reflections), and any three-dimensional object can be classified as ***belonging*** to one of these point groups. The point group symmetry of an object is determined from the following:

$\boldsymbol{C}_n$	one n-fold rotation axis,
$\boldsymbol{C}_{n\mathrm{v}}$	one n-fold rotation axis and n reflection planes containing this axis,
$\boldsymbol{C}_{n\mathrm{h}}$	one n-fold rotation axis and one reflection plane perpendicular to this axis,
$\boldsymbol{D}_n$	one n-fold rotation axis and n twofold rotation axes perpendicular to it,
$\boldsymbol{D}_{n\mathrm{d}}$	those of $\boldsymbol{D}_n$ plus n reflection planes containing the n-fold rotation axis and bisecting the angles between the n twofold rotation axes,
$\boldsymbol{D}_{n\mathrm{h}}$	those of $\boldsymbol{D}_n$ plus a reflection plane perpendicular to the n-fold rotation axis,
$\boldsymbol{S}_n$	one alternating axis of symmetry (about which rotation by $2\pi/n$ radians followed by reflection in a plane perpendicular to the axis is a symmetry operation).

The point groups $\boldsymbol{T}_\mathrm{d}$, $\boldsymbol{O}_\mathrm{h}$, and $\boldsymbol{I}_\mathrm{h}$ consist of all rotation, reflection, and rotation-reflection symmetry operations of a regular tetrahedron, cube, and icosahedron, respectively (the rotational subgroups of these point groups are called $\boldsymbol{T}$, $\boldsymbol{O}$, and $\boldsymbol{I}$, respectively). The point group $\boldsymbol{K}_\mathrm{h}$ consists of all the rotation, reflection, and rotation-reflection symmetry operations of a sphere.

4.4 THE POINT GROUP SYMMETRY OF MOLECULES

If a molecule has a unique equilibrium nuclear configuration then we can determine the point group symmetry of the equilibrium molecular structure. For example, the nuclei of a CH_3F molecule in the equilibrium configuration of its electronic ground state form a structure with $\boldsymbol{C}_{3\mathrm{v}}$ point group symmetry; the C-F bond being the threefold rotation axis and the H-C-F planes the reflection planes. The CH_3F molecule is said to have $\boldsymbol{C}_{3\mathrm{v}}$ point group symmetry in its electronic ground state.

Problem 4-1. What is the point group symmetry of the ethylene molecule in its electronic ground state (see Fig. 1-2 on page 17)?

Answer. The equilibrium molecular structure of the ethylene molecule has three twofold rotation axes: one (the z axis) along the C-C bond, one (the y axis) perpendicular to the z axis and in the molecular plane, and one (the x axis) that is perpendicular to both the z and y axes. The xy, yz, and xz planes are reflection symmetry planes so that the point group symmetry is $\boldsymbol{D}_{2\mathrm{h}}$. The elements in the $\boldsymbol{D}_{2\mathrm{h}}$ point group of ethylene are (where i is the product $C_{2z}\sigma_{xy}$)

$$\{E, C_{2x}, C_{2y}, C_{2z}, i, \sigma_{xy}, \sigma_{yz}, \sigma_{xz}\}. \tag{4-4}$$

Examples of some molecular point group symmetries are:

$\boldsymbol{C}_\mathrm{s}$	the HDO molecule (a monodeuterated water molecule),
$\boldsymbol{C}_\mathrm{2v}$	the H_2O molecule,
$\boldsymbol{C}_\mathrm{2h}$	the trans C(HF)C(HF) molecule (*trans*-1,2-difluoroethylene),
$\boldsymbol{C}_\mathrm{3v}$	the CH_3F molecule,
$\boldsymbol{C}_{\infty\mathrm{v}}$	the HCN molecule,
$\boldsymbol{D}_\mathrm{2d}$	the CH_2CCH_2 molecule (allene),
$\boldsymbol{D}_\mathrm{2h}$	the CH_2CH_2 molecule (ethylene),
$\boldsymbol{D}_\mathrm{3d}$	the CH_3CH_3 molecule in its "staggered" conformation (ethane),
$\boldsymbol{D}_\mathrm{3h}$	the BF_3 molecule,
$\boldsymbol{D}_\mathrm{6h}$	the C_6H_6 molecule (benzene),
$\boldsymbol{D}_{\infty\mathrm{h}}$	the CO_2 molecule,
$\boldsymbol{T}_\mathrm{d}$	the CH_4 molecule (methane),
$\boldsymbol{O}_\mathrm{h}$	the SF_6 molecule, and
$\boldsymbol{I}_\mathrm{h}$	the C_{60} molecule (buckminsterfullerene).

In setting up these groups we treat the molecule as a macroscopic object that is static at its equilibrium geometry. However, in applications the groups are used (in a similar way to the way we use the MS group) to label molecular states where these states arise from a quantum mechanical treatment of the dynamics of the molecule. The criteria used to set up the point group, and the way we use it, seem to be totally at odds with each other. However, by starting from the MS group of a molecule, and neglecting the effect of its elements on the rotational and nuclear spin coordinates, we will discover what the elements of a point group really are when applied to interpret the quantum mechanical dynamics of a molecule. They do not involve bodily rotations of the molecule, with or without reflection of the complete molecule in a plane, as a naive interpretation suggests, and we introduce the name 'molecular point group' to distinguish it from the geometrically defined point group of a macroscopic object.

4.5 RELATING ROTATION GROUPS, POINT GROUPS AND MS GROUPS

Each operation of the MS group of a molecule can affect the coordinates of the nuclei and electrons in the molecule. It is convenient to represent the molecular coordinates[2] as being of several types:

(a) The vibrational and electronic (vibronic) coordinates. These are the vibrational displacement coordinates of the nuclei away from their positions at equilibrium, the coordinates of the electrons in the molecule fixed (x, y, z) axis system, and the electron spin coordinates,

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[2] The molecule fixed xyz axes and the Euler angles that we mention here will be discussed at length in Chapter 10.

(b) The rotational coordinates. These are three angles (the Euler angles θ, ϕ and χ) that specify the orientation of the molecule (i.e., the orientation of the molecule fixed xyz axes) in space, and
(c) The nuclear spin coordinates.

Each operation O of the MS group will in general change all these coordinates, and we can write

$$O = O_a O_b O_c. \tag{4-5}$$

In Eq. (4-5) O_a is an operation that produces the change in vibronic coordinates caused by O, O_b is an operation that produces the change in the rotational coordinates caused by O, and O_c is an operation that produces the nuclear spin permutation caused by O. Any of these operations could be an identity operation for which we use the notation E, R^0, and p_0, respectively. The three operations O_a, O_b and O_c commute with each other so the order in which they are written is immaterial in describing the effect of O. We break down the effect of an MS group operation in this way because it helps us to relate it to the effect of molecular point group operations and molecular rotation group operations.

We will use the water molecule as an example, and its MS group is the group $C_{2v}(\mathrm{M}) = \{E, (12), E^*, (12)^*\}$, where we label the protons 1 and 2. For the water molecule it can be shown (as we will now see) that Eq. (4-5) for each operation of the MS group can be written as follows:

$$E = ER^0 p_0, \tag{4-6a}$$

$$(12) = C_{2x} R_x{}^\pi p_{12}, \tag{4-6b}$$

$$E^* = \sigma_{xz} R_y{}^\pi p_0, \tag{4-6c}$$

and

$$(12)^* = \sigma_{xy} R_z{}^\pi p_{12}, \tag{4-6d}$$

where p_{12} permutes the spins of H_1 and H_2.

In Figs. 4-5, 4-6, and 4-7 we represent the effect of the operations O, O_a, O_b, and O_c on the water molecule for $O = (12)$, E^*, and $(12)^*$, respectively [see also Bunker and Papoušek (1969)]. In each molecular figure the three black dots represent the instantaneous position of the oxygen nucleus and of the hydrogen nuclei in a rotating and vibrating water molecule. The solid arrows passing through the protons represent the space quantized nuclear spins. The open circles represent the positions of the nuclei in the equilibrium configuration from which the molecule is distorted and (x, y, z) are the molecule fixed axes.[3] The 'e' is an electron with its spin marked by an arrow through it, and the + or − above the 'e' indicates whether the electron is above or below the plane of the paper.

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[3] In each molecular figure the location of the molecule fixed (x, y, z) axes, and of the molecule in its equilibrium configuration, is obtained from the instantaneous nuclear coordinates by applying the Eckart equations (see Section 10.2).

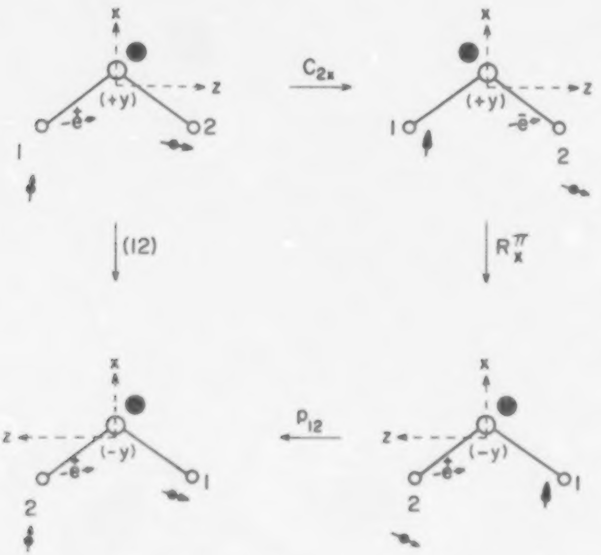

Fig. 4-5. The effect of the successive operations C_{2x}, R_x^π, and p_{12} on a distorted water molecule and the equivalence of this to the permutation (12). The molecule fixed (x, y, z) axes are right handed in all figures.

Figure 4-5 depicts Eq. (4-6b). It shows the successive effects of (a) the molecular point group operation C_{2x} which is defined as rotating the vibrational displacements and electronic coordinates about the x axis through π radians, followed by (b) the molecular rotation operation R_x^π which is a bodily rotation of the molecule about the molecule fixed x axis through π radians, and (c) the operation p_{12} which is the permutation of the nuclear spins. Doing the operations C_{2x}, R_x^π and p_{12} successively is equivalent to the nuclear permutation (12), and the effect of the MS group operation (12) is also shown in Figure 4-5. Figures 4-6 and 4-7 are similar representations of Eqs. (4-6c) and (4-6d). It is very important to notice that the orientation of the molecule fixed axes and the nuclear spins are unaffected by any molecular point group operation.

For nonlinear rigid molecules it turns out that if we determine the expression for each element of the MS group according to Eq. (4-5) then the group of all operations O_a will be the molecular point group. The operations O_b will occur in the molecular rotation group of the molecule, but the group of all operations O_b will sometimes be only a subgroup of the molecular rotation group. It so happens that for the water molecule the group of all operations O_b (i.e., the group $\{R^0, R_x^\pi, R_y^\pi, R_z^\pi\}$) is the molecular rotation group ($\boldsymbol{D}_2$) for the water molecule. The operations O_c will be in a group whose elements only permute the spins (but not the coordinates) of the nuclei; we do not discuss this group (this *nuclear spin permutation group* could be used for classifying nuclear spin

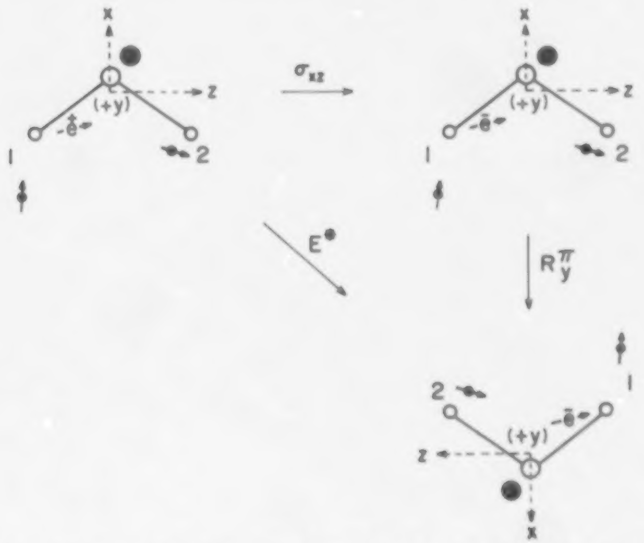

Fig. 4-6. The effect of the successive operations σ_{xz} and R_y^π on a distorted water molecule, and the equivalence of this to the inversion E^*. The molecule fixed (x, y, z) axes are right handed in all figures.

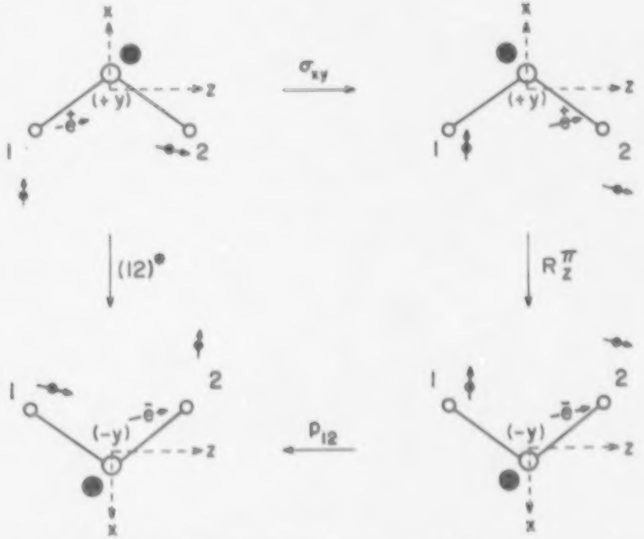

Fig. 4-7. The effect of the successive operations σ_{xy}, R_z^π, and p_{12} on a distorted water molecule, and the equivalence of this to the permutation-inversion operation $(12)^*$. The molecule fixed (x, y, z) axes are right handed in all figures.

states). It seems quite amazing that setting up the MS group as the subgroup of all feasible elements of the CNPI group leads to a group for a nonlinear rigid molecule where the effects of the elements on the vibronic variables is exactly duplicated by the effect of the elements of the molecular point group that was derived by considering the geometry of the equilibrium structure of the molecule. But that is the way it is. The relation between the MS group and the molecular point group will be discussed more in Section 12.6.2.

The point group of a centrosymmetric molecule, such as ethylene, contains the point group operation i, and this operation merits special attention. In the molecular symmetry group of a centrosymmetric molecule there is always present an operation that we will call O_i; the operation O_i is a permutation inversion operation that can be written as

$$O_i = (\mathrm{AA}')(\mathrm{BB}')(\mathrm{CC}'')\cdots(\mathrm{NN}')^* \tag{4-7}$$

where AA′, BB′, CC″, . . . , NN′ are all pairs of identical nuclei that, in the equilibrium configuration, are located symmetrically about the nuclear center of mass. For the ethylene molecule labeled as in Table A-9 we have

$$O_i = (14)(23)(56)^*, \tag{4-8}$$

for the ethane molecule labeled as in Table A-13 we have

$$O_i = (14)(26)(35)(78)^*, \tag{4-9}$$

and for the carbon dioxide molecule labeled as in Table A-18 we have

$$O_i = (12)^*. \tag{4-10}$$

The operation O_i does not change the positions in space of the nuclei when they are in the equilibrium configuration of the centrosymmetric molecule and as a result the operation O_i does not change the Euler angles. The vibronic coordinates are inverted and the nuclear spins of the pairs of nuclei AA′, BB′, CC″, . . . , NN′ are interchanged by O_i. Thus the molecular symmetry group operation O_i and the molecular point group operation i are related by [compare with Eq. (4-6c)]

$$O_i = iR^0 p_{(\mathrm{AA}')(\mathrm{BB}')(\mathrm{CC}'')\cdots(\mathrm{NN}')} \tag{4-11}$$

where $p_{(\mathrm{AA}')(\mathrm{BB}')(\mathrm{CC}'')\cdots(\mathrm{NN}')}$ is the permutation of the nuclear spins. The point group operation i is not the same as the operation E^* and it does not give the parity label of the state; it gives the g or u label on the vibronic states of a centrosymmetric molecule.

Linear molecules are special. The point group of an unsymmetrical linear molecule such as HCN is the group $\boldsymbol{C}_{\infty v}$, and that of a symmetrical linear molecule such as CO_2 is $\boldsymbol{D}_{\infty h}$; these groups are of infinite order. However, the MS group of an unsymmetrical linear molecule is $\{E, E^*\}$, and that of a symmetrical linear molecule is $\{E, (p), E^*, (p)^*\}$ where (p) is the permutation of all pairs of identical nuclei that, in the equilibrium configuration, are symmetrically located about the center of the molecule [see the answer to Problem 3-1 (vii) on page 40]. Clearly for a linear rigid molecule the point group and the MS group do not have the same number of elements. This means that while the rovibronic states (rotation levels) are labeled using the MS group, the vibronic states are labeled using the point group. To obtain one group that can be used for both purposes requires that we introduce the 'extended MS group of a linear molecule', and this is discussed in Section 17.4.

Equation (4-5) can be reversed so that the molecular point group operation is the subject, i.e.,

$$O_a = O O_c^{-1} O_b^{-1}. \tag{4-12}$$

We can now generalize the concept of the molecular point group to nonrigid molecules that have no unique point group symmetry. We call the group that is a generalization of the molecular point group the *molecular vibronic group* and its elements are obtained as follows. Having obtained the MS group (or, when necessary, the extended MS group of a nonrigid molecule as we discuss in Chapter 15), each element O is converted to an element of the molecular vibronic group by undoing (or just neglecting) the changes in Euler angles and the permutation of the nuclear spins that it causes. This is achieved in Eq. (4-12) where O_b^{-1} "removes" the Euler angle change and O_c^{-1} "removes" the nuclear spin permutation. For a rigid non-linear molecule this would be the way to obtain the molecular point group, and Eq. (4-12) provides a way of introducing the molecular point group after beginning by defining the MS group. In general the molecular vibronic group is used to classify vibrational and electronic states and to study vibronic interactions without having to bother about the Euler angles or the nuclear spins.

As well as introducing the vibronic group as a generalization of the molecular point group for the classification of the vibronic states of nonrigid molecules we can also introduce the molecular rotation-contortion group as a generalization of the molecular rotation group. The molecular rotation-contortion group is a group of elements each of which transforms the rotational and contortional variables and which commutes with the rotation–contortion Hamiltonian $\hat{H}_{rc}$ [see Eq. (1[illegible]-5)]. This group can be obtained from the MS (or extended MS) group by neglecting the effect of each element on the vibronic coordinates and nuclear spin coordinates. Such groups have been used by microwave spectroscopists for many years [see, for example, Myers and Wilson (1960)], and a general discussion is given of their determination by Bauder, Meyer, and Günthard (1974); these latter authors call such groups *isometric* groups.

We have been very careful to distinguish between 'the point group' and 'the molecular point group'; the former is a group of overall rotations with and without complete reflection of a rigid body, and the latter is a group of rotations with and without reflection of electronic coordinates and vibrational displacements in a molecule. In the development of the idea of the MS group the papers by Hougen are crucial [Hougen (1962c,1963)]. For nonlinear rigid molecules he introduced 'the full point group' by combining appropriate rotation operations with each element of the molecular point group (which itself only affects vibronic coordinates) for the purpose of classifying rovibronic states. This has lead to an unfortunate ambiguity in the literature as to what a 'point group' is. Some authors use the term 'point group' for what we call the MS group. This is unfortunate since it is important to distinguish carefully between what we call the MS group and what we call the molecular point group. If one looks at what the elements of the MS group do to a molecule then it really does not seem very logical to call them elements of a point group. For example, in Fig. 4-7 the effect of the MS group operation $(12)^*$ is depicted. This is quite clearly not simply a reflection of the molecule in the xy plane. Also when one considers nonrigid molecules there is no way that the MS group can be called a point group, and so this nomenclature lacks the necessary generality.

Following on from this ambiguous use of the term 'point group' is the so-called "rotational subgroup of the point group" that is said to be used in determining the nuclear spin statistical weights of the levels of rigid nonlinear molecules. The real rotational subgroup of the molecular point group consists only of the rotation operations from the point group, e.g., it is $\{E, C_{2x}\}$ for the $\boldsymbol{C}_{2\mathrm{v}}$ group for the water molecule. Such operations do not permute nuclei and so the statistical formulas that are used to determine nuclear spin statistical weights cannot be applied to their result. However, what is called the "rotational subgroup of the point group" is really the permutation subgroup of the molecular symmetry group. The use of this group, and the use of the molecular symmetry group, in determining statistical weights is discussed in Chapter 8.

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5

Representations and Character Tables

Matrices and matrix groups are introduced, and the concepts of isomorphism and homomorphism are defined. Matrix groups form representations of other groups, and we focus particular attention on the definition of irreducible and inequivalent representations. We discuss the class structure and character table of a group. Direct and semidirect group products are defined, and we discuss the special structure of the character table of a direct product group. Correlation tables and reverse correlation tables are explained at the end of the chapter.

5.1 MATRICES AND MATRIX GROUPS

It is necessary to understand what matrices are and to be able to multiply them together in order to be able to work with matrix groups, and we summarize some important definitions here. A matrix is an array of numbers (called elements) arranged in rows and columns; for example

$$D = \begin{bmatrix} 2 & 3 \\ 4 & 5 \end{bmatrix} \qquad (5\text{-}1)$$

is a matrix. The matrix in Eq. (5-1) has two rows and two columns, and since it has the same number of rows as columns it is said to be a ***square matrix;*** matrices are not necessarily square. An $n \times n$ square matrix (having n rows and n columns) is said to be n-dimensional. In a general matrix, A say, the element occurring at the intersection of the ith row and jth column is called A_{ij}. In the matrix in Eq. (5-1) we have

$$\begin{aligned} D_{11} &= 2, \quad D_{12} = 3, \\ D_{21} &= 4, \quad D_{22} = 5. \end{aligned} \qquad (5\text{-}2)$$

In applying group theory to molecules it is often be necessary to multiply matrices together, and we must explain how the product of two matrices is defined. The product of an $n \times m$ matrix A (having n rows and m columns) and an $m \times q$ matrix B in the order AB is an $n \times q$ matrix C where the ijth element of C is given by

$$C_{ij} = \sum_{k=1}^{m} A_{ik} B_{kj}. \tag{5-3}$$

Notice that for the multiplication AB to be defined the number of columns in A must be equal to the number of rows in B. The product of an $n \times n$ square matrix A with a column matrix (to the right of A) of n elements is another column matrix with n elements. The product of an $n \times n$ square matrix A with a row matrix (to the left of A) of n elements is another row matrix with n elements. Three examples follow to help in the understanding of this:

A square matrix times a square matrix,

$$\begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}\begin{bmatrix} 5 & 6 \\ 7 & 8 \end{bmatrix} = \begin{bmatrix} 1\times 5+2\times 7 & 1\times 6+2\times 8 \\ 3\times 5+4\times 7 & 3\times 6+4\times 8 \end{bmatrix} = \begin{bmatrix} 19 & 22 \\ 43 & 50 \end{bmatrix}. \tag{5-4}$$

A square matrix times a column matrix,

$$\begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}\begin{bmatrix} 5 \\ 7 \end{bmatrix} = \begin{bmatrix} 1\times 5+2\times 7 \\ 3\times 5+4\times 7 \end{bmatrix} = \begin{bmatrix} 19 \\ 43 \end{bmatrix}. \tag{5-5}$$

A row matrix times a square matrix,

$$\begin{bmatrix} 1 & 2 \end{bmatrix}\begin{bmatrix} 5 & 6 \\ 7 & 8 \end{bmatrix} = \begin{bmatrix} 1\times 5+2\times 7 & 1\times 6+2\times 8 \end{bmatrix} = \begin{bmatrix} 19 & 22 \end{bmatrix}. \tag{5-6}$$

We can also take the product in Eq. (5-4) the other way around to get:

$$\begin{bmatrix} 5 & 6 \\ 7 & 8 \end{bmatrix}\begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix} = \begin{bmatrix} 5\times 1+6\times 3 & 5\times 2+6\times 4 \\ 7\times 1+8\times 3 & 7\times 2+8\times 4 \end{bmatrix} = \begin{bmatrix} 23 & 34 \\ 31 & 46 \end{bmatrix}. \tag{5-7}$$

We see that matrix multiplication, like permutation multiplication or the multiplication of the elements of rotation groups or point groups, is not necessarily commutative. However, matrix multiplication is associative.

If we multiply an n-dimensional square matrix A by an n-dimensional square matrix E having 1 in all diagonal positions ($E_{ii} = 1$), and zero in all off-diagonal positions ($E_{ij} = 0$ for $i \neq j$), the result is still A. That is the matrix E plays the role in matrix multiplication that unity plays in the ordinary algebraic multiplication of numbers, and such a matrix is called an n-dimensional *unit matrix*. Borrowing the language of ordinary algebraic multiplication we say that if the product of two $n \times n$ matrices is the n-dimensional unit matrix then one matrix is the inverse of the other. For example,

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \tag{5-8}$$

and the matrices on the left hand side in this equation are, therefore, the inverse of each other. These two matrices are also equal to the *transpose* of each other, where the transpose of a matrix A, say, is obtained by interchanging each element A_{ij} with the element A_{ji}, and the matrix is written $\tilde{A}$. Thus from Eq. (5-1) we have

$$\tilde{D} = \begin{bmatrix} 2 & 4 \\ 3 & 5 \end{bmatrix}. \tag{5-9}$$

If a matrix is equal to its transpose then the matrix is *symmetric*, and if a matrix is equal to the inverse of its transpose then the matrix is *orthogonal*. Each of the two matrices on the left hand side in Eq. (5-8) is orthogonal.

The *Hermitian conjugate* (or *conjugate transpose*) $A^\dagger$ of a matrix A is obtained by taking the complex conjugate of the transpose of the matrix. Thus

$$A^\dagger = (\tilde{A})^* \tag{5-10}$$

and

$$(A^\dagger)_{ij} = A^*_{ji}. \tag{5-11}$$

A matrix that is equal to its Hermitian conjugate is *Hermitian* and a matrix that is equal to the inverse of its Hermitian conjugate is *unitary*.

The sum of the diagonal elements of a square matrix is the *trace* of the matrix; the Greek letter chi (χ) is used for it. From Eqs. (5-1) and (5-9) we have

$$\chi(D) = \chi(\tilde{D}) = 7. \tag{5-12}$$

The *determinant* of an $n \times n$ square matrix A is given by

$$|A| = \sum (-1)^h A_{1r_1} A_{2r_2} A_{3r_3} \dots A_{nr_n}, \tag{5-13}$$

where the summation is over all $n!$ possible permutations of the order of the r_i. The $(n!)/2$ terms in the sum involving an even permutation of the order of the r_i from the order $123 \dots n$ have h even, and the $(n!)/2$ terms involving an odd permutation have h odd. For the matrix D in Eq. (5-1) the determinant involves two terms: the first is $D_{11}D_{22}$ having h even, and the second is $D_{12}D_{21}$ having h odd. Thus we have

$$|D| = \begin{vmatrix} 2 & 3 \\ 4 & 5 \end{vmatrix} = (2 \times 5) - (3 \times 4) = -2. \tag{5-14}$$

In Table 5-1 we summarize all the definitions introduced in this section.

Table 5-1

Summary of definitions used in matrix algebra

Notation	Meaning
Transpose $\tilde{A}$	$(\tilde{A})_{ij} = A_{ji}$
Symmetric matrix	$A = \tilde{A}$, i.e., $A_{ij} = A_{ji}$
Hermitian conjugate $A^\dagger$	$(A^\dagger)_{ij} = A^*_{ji} = (\tilde{A})^*_{ij}$
Hermitian matrix	$A = A^\dagger$, i.e., $A_{ij} = A^*_{ji}$
Unit matrix E	$E_{ij} = 0$ if $i \neq j$ and $E_{ij} = 1$ if $i = j$
Inverse A^{-1}	$AA^{-1} = A^{-1}A = E$
Orthogonal matrix	$A^{-1} = \tilde{A}$, i.e., $(A^{-1})_{ij} = A_{ji}$
Unitary matrix	$A^{-1} = A^\dagger$, i.e., $(A^{-1})_{ij} = A^*_{ji}$
Diagonal matrix	$A_{ij} = 0$ if $i \neq j$
Trace χ of matrix A	$\chi = \sum_i A_{ii}$
Determinant[a] of matrix A	$\lvert A \rvert = \sum (-1)^h A_{1r_1} A_{2r_2} A_{3r_3} \ldots A_{nr_n}$
Kronecker delta δ	$\delta_{ij} = 0$ if $i \neq j$ and $\delta_{ij} = 1$ if $i = j$

[a] To use this equation see the text following Eq. (5-13).

Problem 5-1. Consider the following two-dimensional square matrix,

$$M = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}, \tag{5-15}$$

where $i^2 = -1$. Is this matrix unitary? What is the trace of this matrix?

Answer. To test if M is unitary we must see if

$$MM^\dagger = E, \tag{5-16}$$

where E is the 2×2 unit matrix. To form $M^\dagger$ we form the transpose of M and take the complex conjugate.

$$\tilde{M} = \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} \tag{5-17}$$

and

$$M^\dagger = (\tilde{M})^* = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}. \tag{5-18}$$

We see that

$$M^\dagger = M \tag{5-19}$$

and therefore M is Hermitian. Testing Eq. (5-16) we have

$$MM^{\dagger} = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} = \begin{bmatrix} 1 & i \\ -i & 1 \end{bmatrix}. \tag{5-20}$$

Thus

$$MM^{\dagger} \neq \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \tag{5-21}$$

and M is not unitary. The trace of M is the sum of the diagonal elements, i.e.,

$$\chi(M) = \sum_{j} M_{jj} = 1/\sqrt{2} + 1/\sqrt{2} = \sqrt{2}. \tag{5-22}$$

We can define a ***matrix group***. A matrix group is a set of square matrices (all with the same dimension) that obey the group axioms; in a matrix group the operation of multiplication is matrix multiplication and the identity is the unit matrix. The following set of six matrices is an example of a two-dimensional matrix group, and we call the group Γ_3 (the subscript 3 has no special significance but it is a useful notation in this chapter):

$$\left\{ \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}, \right.$$
$$\left. \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}, \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}, \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \right\}. \tag{5-23}$$

The reader can form the multiplication table of this group and confirm that the four group axioms are satisfied. From Eq. (5-8) we see that the last two matrices in this group are the inverse (or reciprocal) of each other. The first four matrices in the group are symmetric, and since they are also self-reciprocal they are orthogonal. In this matrix group, therefore, all the matrices are orthogonal.

5.2 ISOMORPHISM AND FAITHFUL REPRESENTATIONS

In Eqs. (1-46) and (4-1) we introduce the groups $\boldsymbol{S}_3$ (a permutation group) and $\boldsymbol{D}_3$ (a rotation group), respectively. These groups, together with the matrix group Γ_3 of Eq. (5-23), are used to explain the concept of isomorphism. We can make the following one-to-one correspondences between the elements of the $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$ groups

$$\begin{gathered} E - E, \\ (12) - C_{2a}, \quad (23) - C_{2b}, \quad (13) - C_{2c}, \\ (123) - C_{3d}, \quad (132) - C_{3d}^{2}. \end{gathered} \tag{5-24}$$

Each element in $\boldsymbol{S}_3$ has a partner in the $\boldsymbol{D}_3$ group according to Eq. (5-24). We have chosen the partners in Eq. (5-24) in a special way so that if we replace each element of $\boldsymbol{S}_3$ in the multiplication table for $\boldsymbol{S}_3$ (Table 1-1) by its partner in the $\boldsymbol{D}_3$ group [according to Eq. (5-24)] then we obtain the multiplication table of the $\boldsymbol{D}_3$ group (see Table 4-1). These two multiplication tables have the same structure, and the $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$ groups are therefore said to be isomorphic. For example, in the $\boldsymbol{S}_3$ group we have the product [see Eq. (1-22)]

$$(132)(23) = (13), \tag{5-25}$$

from which, by replacing each element by its partner according to Eq. (5-24), we obtain

$$C_{3d}^2 C_{2b} = C_{2c}, \tag{5-26}$$

and this is true (see Table 4-1). Formally two groups are isomorphic if the elements of one $(A, B, C, \ldots)$ correspond to (or can be *mapped* onto) the elements of the other $(\bar{A}, \bar{B}, \bar{C}, \ldots)$ in a one-to-one fashion $(A - \bar{A}, B - \bar{B}, C - \bar{C}, \ldots)$ so that from $AB = C$ it can be inferred that $\bar{A}\bar{B} = \bar{C}$, etc. Clearly isomorphic groups must have the same order, but groups of the same order are not necessarily isomorphic. The best way to test if two groups are isomorphic is to look at their multiplication tables and to check that everywhere A occurs in the one, $\bar{A}$ occurs in the other, similarly for B and $\bar{B}$, etc.

The matrix group Γ_3 introduced in Eq. (5-23) is isomorphic to both the $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$ groups, and the mapping is as follows:

$$\begin{array}{llll}
\boldsymbol{S}_3: & E & (12) & (23) \\
\boldsymbol{D}_3: & E & C_{2a} & C_{2b} \\
\Gamma_3: & \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} & \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} \\
\\
\boldsymbol{S}_3: & (13) & (123) & (132) \\
\boldsymbol{D}_3: & C_{2c} & C_{3d} & C_{3d}^2 \\
\Gamma_3: & \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} & \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} & \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}.
\end{array} \tag{5-27}$$

A matrix group that is isomorphic to another group is said to form a faithful representation of that group. Thus the matrix group Γ_3 forms a faithful representation of the $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$ groups. Using the mapping of Eq. (5-27), we see that Eqs. (5-25) and (5-26) map onto the product

$$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}, \tag{5-28}$$

and Eq. (1-23) maps onto the product

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \tag{5-29}$$

in the matrix group. The multiplication table of this matrix group can be obtained by replacing each element in the multiplication table of the $\boldsymbol{S}_3$ group in Table 1-1 (or of the $\boldsymbol{D}_3$ group in Table 4-1) by its partner in the matrix group using the mapping of Eq. (5-27).

5.3 HOMOMORPHISM AND UNFAITHFUL REPRESENTATIONS

Homomorphism is similar to isomorphism except that instead of the correspondence being a one-to-one correspondence between elements of groups having the same order, it is a many-to-one correspondence between elements of groups having different orders. The larger group is said to be homomorphic onto the smaller group. For example, the group $\boldsymbol{D}_3$ is homomorphic onto the $\boldsymbol{S}_2$ group $\{E, (12)\}$ with the following correspondences:

$$\begin{array}{ll} \boldsymbol{D}_3\text{:} & \underbrace{E \quad C_{3d} \quad C_{3d}^2}_{E} \quad \underbrace{C_{2a} \quad C_{2b} \quad C_{2c}}_{(12)} \\ \boldsymbol{S}_2\text{:} & \end{array} \tag{5-30}$$

If, in the multiplication table of $\boldsymbol{D}_3$ (Table 4-1), the elements E, C_{3d}, and C_{3d}^2 are replaced by E (of $\boldsymbol{S}_2$), and C_{2a}, C_{2b}, and C_{2c} by (12), we obtain the multiplication table of $\boldsymbol{S}_2$ (nine times over).

Many-to-one mappings of $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$ onto two one-dimensional matrix groups can be made. These two groups are

$$\Gamma_1 : \quad \{1\} \tag{5-31}$$

and

$$\Gamma_2 : \quad \{1, -1\}. \tag{5-32}$$

These are one-dimensional matrix groups, and matrix multiplication is simply ordinary algebraic multiplication in this case. The homomorphic mapping of $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$ onto these matrix groups is shown below.

$$\begin{array}{lcccccc} \boldsymbol{D}_3 : & E & C_{2a} & C_{2b} & C_{2c} & C_{3d} & C_{3d}^2 \\ \boldsymbol{S}_3 : & E & (12) & (23) & (13) & (123) & (132) \\ \\ \Gamma_1 : & 1 & 1 & 1 & 1 & 1 & 1 \\ \Gamma_2 : & 1 & -1 & -1 & -1 & 1 & 1 \end{array} \tag{5-33}$$

If a group is homomorphic onto a matrix group then the matrix group is said to form an unfaithful representation of the group; thus Γ_1 and Γ_2 each form unfaithful representations of $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$.

5.4 EQUIVALENT AND IRREDUCIBLE REPRESENTATIONS

We have introduced the three representations Γ_1, Γ_2, and Γ_3 of the groups $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$. We can use these representations in two different ways to construct others, but these three are special in that they are *irreducible* and also all other irreducible representations of $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$ are *equivalent* to these. We must now define the terms irreducible and equivalent, and show how other representations can be formed from these three.

5.4.1 Equivalent representations

One way of forming a new representation from the Γ_3 representation involves forming an equivalent representation. We could subject each of the matrices of the representation Γ_3 to the same *similarity transformation*, i.e., post multiply each matrix of Γ_3 by a 2 × 2 matrix, A say, and then premultiply each result by the inverse of A: thus a matrix M_r in Γ_3 would be changed to $A^{-1}M_rA$ and, since matrix multiplication is associative,

$$(A^{-1}M_rA)(A^{-1}M_sA) = A^{-1}M_r(AA^{-1})M_sA = A^{-1}M_rM_sA. \qquad (5\text{-}34)$$

The new matrix group is isomorphic to Γ_3 with the mapping of M_r onto $A^{-1}M_rA$, etc. The new set of matrices is, therefore, also isomorphic to $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$ and it forms a faithful representation of them. Two representations related by a similarity transformation are said to be equivalent, and for our applications in molecular physics equivalent representations are usually not distinguished.

Problem 5-2. Post multiply each matrix of Γ_3 by the matrix

$$A = \begin{bmatrix} 1 & 1 \\ 3 & 4 \end{bmatrix}$$

and premultiply by

$$A^{-1} = \begin{bmatrix} 4 & -1 \\ -3 & 1 \end{bmatrix}.$$

Test that the new representation is isomorphic to Γ_3. What do you notice about the traces of each of the matrices in the new representation compared to those of the matrices in the group Γ_3?

Answer. The new matrix group obtained from Γ_3 in the order that the matrices are given in Eq. (5-27) is

$$\left\{\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \begin{bmatrix} 7 & 8 \\ -6 & -7 \end{bmatrix}, \begin{bmatrix} -\frac{7}{2} + \frac{11\sqrt{3}}{2} & -4 + \frac{15\sqrt{3}}{2} \\ 3 - 4\sqrt{3} & \frac{7}{2} - \frac{11\sqrt{3}}{2} \end{bmatrix}, \begin{bmatrix} -\frac{7}{2} - \frac{11\sqrt{3}}{2} & -4 - \frac{15\sqrt{3}}{2} \\ 3 + 4\sqrt{3} & \frac{7}{2} + \frac{11\sqrt{3}}{2} \end{bmatrix}, \begin{bmatrix} -\frac{1}{2} + \frac{13\sqrt{3}}{2} & \frac{17\sqrt{3}}{2} \\ -5\sqrt{3} & -\frac{1}{2} - \frac{13\sqrt{3}}{2} \end{bmatrix}, \begin{bmatrix} -\frac{1}{2} - \frac{13\sqrt{3}}{2} & -\frac{17\sqrt{3}}{2} \\ 5\sqrt{3} & -\frac{1}{2} + \frac{13\sqrt{3}}{2} \end{bmatrix}\right\}. \tag{5-35}$$

These matrices look complicated compared to those that make up the representation Γ_3, but it is straightforward (although tedious) to show by working out the multiplication table, that this matrix group is isomorphic to the group Γ_3. This matrix group, therefore, forms a representation of the $\boldsymbol{S}_3$ and $\boldsymbol{D}_3$ groups. Equation (1-23), for example, maps onto

$$\begin{bmatrix} -\frac{7}{2} + \frac{11\sqrt{3}}{2} & -4 + \frac{15\sqrt{3}}{2} \\ 3 - 4\sqrt{3} & \frac{7}{2} - \frac{11\sqrt{3}}{2} \end{bmatrix} \begin{bmatrix} -\frac{1}{2} - \frac{13\sqrt{3}}{2} & -\frac{17\sqrt{3}}{2} \\ 5\sqrt{3} & -\frac{1}{2} + \frac{13\sqrt{3}}{2} \end{bmatrix} = \begin{bmatrix} 7 & 8 \\ -6 & -7 \end{bmatrix}. \tag{5-36}$$

Part of the reason why the matrices in Γ_3 look simpler than those in the new representation of Eq. (5-35) is that each of the matrices in Γ_3 is orthogonal. In fact it is possible to choose a similarity transformation so that all the matrices in any representation are unitary, and this is always done. Unitary representations are used in the application of representation theory to molecules.

The trace of a matrix in a representation is called the *character* [but still denoted χ] of the matrix. In the new representation of Eq. (5-35) each matrix has the same character as its partner in the group Γ_3. It is left as an exercise for the reader to show that a similarity transformation does not change the character of a matrix, i.e., that the characters of M_r and $A^{-1}M_rA$ are identical. As a result we see that equivalent representations have the same characters.

5.4.2 Irreducible representations

Another way of forming a new representation of $\boldsymbol{S}_3$ or $\boldsymbol{D}_3$ from the representations Γ_1, Γ_2, and Γ_3 is by combining them to form what is called a *reducible* representation. For example, the representations Γ_2 and Γ_3 can be combined to form the following reducible three-dimensional representation [where the matrices are in the same order as in Eq. (5-27)]:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix}, \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{5-37}$$

Each of the matrices in the representation given in Eq. (5-37) is said to be *block diagonal*. A block diagonal matrix is such that the nonzero elements occur in blocks along the diagonal of the matrix, and in Eq. (5-37) each matrix consists of an upper left 2×2 block and a lower right 1×1 block, with zeros in the off diagonal positions that connect the elements in one block with those of the other. Block diagonal matrices can consist of more than two blocks along the diagonal, for example the matrix

$$\begin{bmatrix} 1 & 2 & 3 & 0 & 0 & 0 & 0 \\ 0 & 5 & 6 & 0 & 0 & 0 & 0 \\ 7 & 4 & 8 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 6 & 5 & 0 & 0 \\ 0 & 0 & 0 & 4 & 3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 8 & 9 \\ 0 & 0 & 0 & 0 & 0 & 1 & 2 \end{bmatrix}$$

is also block diagonal and consists of a 3×3 block and two 2×2 blocks. The reader can use Eq. (5-3) to prove that the product of two block diagonal matrices having the same block structure produces a third block diagonal matrix that has the same block structure. The representation in Eq. (5-37) is said to be in *block diagonal form*, and in such a representation all the matrices must have the same block structure as each other.

The representation of $\boldsymbol{S}_3$ or $\boldsymbol{D}_3$ in Eq. (5-37) has characters that are the sum of the characters of the Γ_2 and Γ_3 representations. If we were to subject the representation to a similarity transformation, to form an equivalent representation, the characters would be the same. If we know the characters of the representations Γ_2 and Γ_3, then by inspecting the characters of this reducible representation (or one that is equivalent to it) we are able to determine how it has been built up.

The fact that the representation in Eq. (5-37) (which we call Γ_{sum}) is made up by combining the Γ_2 and Γ_3 representations is symbolically expressed by writing

$$\Gamma_{\text{sum}} = \Gamma_2 \oplus \Gamma_3. \tag{5-38}$$

For an element R, say, of the $\boldsymbol{D}_3$ or $\boldsymbol{S}_3$ group the character in Γ_{sum} is given by the sum of the characters of the Γ_2 and Γ_3 representations, i.e.,

$$\chi^{\Gamma_{\mathrm{sum}}}[R] = \chi^{\Gamma_2}[R] + \chi^{\Gamma_3}[R], \tag{5-39}$$

where $\chi^{\Gamma_i}[R]$ is the character in the representation Γ_i of the matrix $D^{\Gamma_i}[R]$ that maps onto the element R of the symmetry group.

A representation that cannot be brought into block diagonal form by any similarity transformation applied simultaneously to all the matrices of the representation is said to be irreducible, and for a finite group there are a finite number of inequivalent irreducible representations. It can be shown that the matrix elements $D^{\Gamma_i}[R]_{mn}$ and $D^{\Gamma_j}[R]_{m'n'}$ of the matrices in the irreducible representations Γ_i and Γ_j of any group satisfy the following *orthogonality relation*:

$$\sum_R D^{\Gamma_i}[R]^*_{mn}\sqrt{\frac{l_i}{h}}D^{\Gamma_j}[R]_{m'n'}\sqrt{\frac{l_j}{h}} = \delta_{ij}\delta_{mm'}\delta_{nn'}, \tag{5-40}$$

where h is the order of the group, l_i and l_j are the dimensions of the irreducible representations Γ_i and Γ_j, respectively, and the sum is over all elements R in the group. From Eq. (5-40) it follows that the characters of irreducible representations are orthogonal, i.e.,

$$\sum_R \chi^{\Gamma_i}[R]^*\chi^{\Gamma_j}[R] = h\delta_{ij} \tag{5-41}$$

for two irreducible representations Γ_i and Γ_j.

It turns out that the representations Γ_1, Γ_2, and Γ_3, in Eqs. (5-33) and (5-27), are the only inequivalent irreducible representations of the groups $\boldsymbol{D}_3$ and $\boldsymbol{S}_3$ [see the discussion following Eq. (5-50)]. Therefore, any representation Γ of $\boldsymbol{D}_3$ or $\boldsymbol{S}_3$ can be written

$$\Gamma = a_1\Gamma_1 \oplus a_2\Gamma_2 \oplus a_3\Gamma_3, \tag{5-42}$$

and the characters satisfy

$$\chi^{\Gamma}[R] = a_1\chi^{\Gamma_1}[R] + a_2\chi^{\Gamma_2}[R] + a_3\chi^{\Gamma_3}[R], \tag{5-43}$$

where the a_i are integers.

5.5 REDUCTION OF A REPRESENTATION

Irreducible (and inequivalent) matrix representations play a special role in molecular physics since we are able to use them to label molecular states. This provides a very useful characterization of the state, and in applications we frequently obtain a reducible representation which we need to reduce to its irreducible components. The way that a given representation of a group is reduced to its irreducible components depends only on the characters of the matrices in the representation and on the characters of the matrices in the irreducible representations of the group. For most of the groups of interest to us, the characters of the irreducible representations have been tabulated; such a table is called *the character table* of the group.

To reduce a representation to its irreducible components we can sometimes guess the answer by using Eq. (5-43), but in general we proceed as follows. Suppose that the reducible representation is Γ and that the irreducible representations of the group involved are $\Gamma_1, \Gamma_2, \Gamma_3, \ldots$. We desire to find the integral coefficients a_i, where

$$\Gamma = a_1\Gamma_1 \oplus a_2\Gamma_2 \oplus a_3\Gamma_3 \oplus \cdots \tag{5-44a}$$

and

$$\chi^{\Gamma}[R] = \sum_j a_j \chi^{\Gamma_j}[R], \tag{5-44b}$$

with the sum running over all the irreducible representations of the group. Multiplying Eq. (5-44b) on the right by $\chi^{\Gamma_i}[R]^*$ and summing over R it follows from the character orthogonality relation [Eq. (5-41)] that the a_i are given by

$$a_i = \frac{1}{h}\sum_R \chi^{\Gamma}[R]\chi^{\Gamma_i}[R]^*, \tag{5-45}$$

where h is the order of the group and R runs over all the elements of the group. Since the reduction of a representation depends only on the characters this means that representations having the same characters must be equivalent and that the characters serve to distinguish inequivalent representations.

If we put $i = j$ in Eq. (5-41) we see that for an irreducible representation

$$\sum_R |\chi^{\Gamma_i}[R]|^2 = h, \tag{5-46}$$

which can be used as a test for the irreducibility of a representation. Another result of importance is that the sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group, i.e.,

$$\sum_i l_i^2 = h, \tag{5-47}$$

where the sum is over all irreducible representations of the group; this equation can be used to test if we have all the irreducible representations of a group.

5.6 CONJUGATE ELEMENTS AND CLASSES

The elements of a group can be divided up into a number of classes, and this important idea will now be defined using a matrix group. In a matrix group we can take one matrix, M_r say, and form the product

$$M_s^{-1} M_r M_s = M_p \tag{5-48}$$

with each of the other matrices M_s in the group. A few moments' thought shows that each of the matrices M_p obtained will also be in the group; from the group axioms both $M_r M_s$ and M_s^{-1} are in the group and hence $M_s^{-1}(M_r M_s)$ must also be in the group. Further, since a similarity transformation, such as is performed on M_r in Eq. (5-48), does not change the character of a matrix, then M_r and M_p will have the same character. Two matrices in a matrix group that are related, as are M_r and M_p in Eq. (5-48), by a similarity transformation involving another matrix (M_s here) of the group are said to be *conjugate* and are said to be in the same *class*.

In any group, whether a matrix group or not, we can divide the elements up into classes. Two elements A and B in a group are said to be in the same class if there exists an element, C say, in the group such that

$$C^{-1}AC = B. \tag{5-49}$$

In the $\boldsymbol{S}_3$ group there are three classes,

$$E, \quad [(12),(23),(13)], \quad \text{and} \quad [(123),(132)]. \tag{5-50}$$

Because of the isomorphism [resulting in "parallel" versions of Eq. (5-49)], the class structures of $\boldsymbol{D}_3$ and Γ_3 are the same as that of $\boldsymbol{S}_3$. It can be shown that there are the same number of irreducible (and inequivalent) representations of a group as there are classes in the group. There are, therefore, only three irreducible representations for the groups $\boldsymbol{D}_3$ or $\boldsymbol{S}_3$, and these are Γ_1, Γ_2, and Γ_3 given in Eqs. (5-27) and (5-33).

Problem 5-3. The internal displacement coordinates (bond stretching and angle bending coordinates including a redundancy) of the BF$_3$ molecule can be shown to generate (in a way to be explained in the next chapter) a representation Γ of the $\boldsymbol{S}_3$ group (this group contains all fluorine nuclei permutations and we label the fluorine nuclei 1, 2, and 3). The characters of this representation are as follows

$$\begin{array}{rcccccc} R: & E & (12) & (23) & (13) & (123) & (132) \\ \chi^{\Gamma}[R]: & 7 & 1 & 1 & 1 & 1 & 1 \end{array} \tag{5-51}$$

Use Eq. (5-45) to reduce this representation into the irreducible representations of the $\boldsymbol{S}_3$ group. You can check that the answer is correct by testing to see if Eq. (5-44b) is satisfied.

Answer. Using Eq. (5-45) with

$$\Gamma = a_1\Gamma_1 \oplus a_2\Gamma_2 \oplus a_3\Gamma_3$$

we have

$$\begin{aligned} a_1 &= (1/6)\{\chi^{\Gamma}[E]\chi^{\Gamma_1}[E]^* + \chi^{\Gamma}[(12)]\chi^{\Gamma_1}[(12)]^* + \chi^{\Gamma}[(23)]\chi^{\Gamma_1}[(23)]^* + \cdots\} \\ &= (1/6)(7\times 1 + 1\times 1 + 1\times 1 + 1\times 1 + 1\times 1 + 1\times 1) \\ &= 2, \end{aligned} \tag{5-52}$$

$$\begin{aligned} a_2 &= (1/6)[7\times 1 + 1\times(-1) + 1\times(-1) + 1\times(-1) + 1\times 1 + 1\times 1] \\ &= 1, \end{aligned} \tag{5-53}$$

and

$$\begin{aligned} a_3 &= (1/6)[7\times 2 + 1\times 0 + 1\times 0 + 1\times 0 + 1\times(-1) + 1\times(-1)] \\ &= 2. \end{aligned} \tag{5-54}$$

Thus

$$\Gamma = 2\Gamma_1 \oplus \Gamma_2 \oplus 2\Gamma_3. \tag{5-55}$$

We now test to see if this is correct by using Eq. (5-44b). For the operation E Eq. (5-44b) gives

$$\chi^\Gamma = 7 = 2\times 1 + 1\times 1 + 2\times 2 \tag{5-56}$$

which is correct. For the operations (12), (23), or (13) Eq. (5-44b) gives

$$\chi^\Gamma = 1 = 2\times 1 + 1\times(-1) + 2\times 0 \tag{5-57}$$

which is correct, and for the operations (123) and (132) Eq. (5-44b) gives

$$\chi^\Gamma = 1 = 2\times 1 + 1\times 1 + 2\times(-1) \tag{5-58}$$

which is also correct.

The class structure in a CNP group is simple to determine since it is easy to show that all permutations having the same shape (i.e., consisting of the same number of independent transpositions, independent cycles of three, independent cycles of four, etc.) are in the same class. The class structure of the $\boldsymbol{S}_3$ group, given in Eq. (5-50), is an example. For the complete electron permutation group $\boldsymbol{S}_n^{(e)}$ of an n-electron molecule this observation leads to Young tableau, and these are discussed in Section 9.4.5 in connection with electronic wavefunction calculations. The class structure of a CNPI group follows from that of the CNP group since E^* is in a class on its own. For example, the class structure of the CNPI group of CH_3F [see Eq. (2-12)] is

$$\begin{array}{cccccc} E & (12) & (123) & E^* & (12)^* & (123)^* \\ & (23) & (132) & & (23)^* & (132)^* \\ & (13) & & & (13)^* & \end{array} \tag{5-59}$$

and this group, therefore, has six irreducible representations.

The class structure of a subgroup of a permutation group, or a subgroup of a CNPI group (such as an MS group), is not so easily determined and Eq. (5-49) must be used. However, in an Abelian group multiplication is commutative (as discussed after Problem 1-7 on page 15) so that each element has to be in a class on its own. When multiplication within a group is commutative the right hand side of Eq. (5-49) can never be anything else except A, i.e., if A and C commute

$$C^{-1}AC = C^{-1}CA = A. \tag{5-60}$$

In Problem 1-7 the subgroup $\{E, (123), (132)\}$ of the group $\boldsymbol{S}_3$ was obtained and this is an Abelian group; hence each of the three elements is in a class of its own. Similarly the MS group of ethylene $\boldsymbol{D}_{2h}(M)$, in Eq. (2-15), is Abelian so that this group has eight classes and eight irreducible representations.

5.7 GROUP PRODUCTS

Often a large group $\boldsymbol{G}$ can be expressed as a 'group product' of two of its subgroups $\boldsymbol{A}$ and $\boldsymbol{B}$:

$$\boldsymbol{G} = \boldsymbol{A} \times \boldsymbol{B}. \tag{5-61}$$

This equation indicates that if all elements of $\boldsymbol{A}$ are multiplied by all elements of $\boldsymbol{B}$, then all elements of $\boldsymbol{G}$ are obtained once and only once.

For example, the CNPI group of CH_3F [see Eqs. (2-12) and (5-59)], which we will call $\boldsymbol{G}_{\mathrm{mf}}^{\mathrm{CNPI}}$ (for methyl fluoride) here, can be written as a product of the two subgroups

$$\boldsymbol{A} = \{E, (12), (23), (13), (123), (132)\} \tag{5-62}$$

and

$$\boldsymbol{B} = \{E, E^*\}. \tag{5-63}$$

From Eq. (5-59) it is seen that both subgroups consist of whole classes of the product group $\boldsymbol{G}_{\mathrm{mf}}^{\mathrm{CNPI}}$. The group $\boldsymbol{A}$ contains the three classes given in the first three columns of Eq. (5-59), and the group $\boldsymbol{B}$ consists of the two classes containing E and E^*, respectively.

If $\boldsymbol{H}$ is a subgroup of the group $\boldsymbol{G}$, and $\boldsymbol{H}$ consists of whole classes of $\boldsymbol{G}$, we say that $\boldsymbol{H}$ is an *invariant subgroup* of $\boldsymbol{G}$. Thus, the groups $\boldsymbol{A}$ and $\boldsymbol{B}$ are both invariant subgroups of $\boldsymbol{G}_{\mathrm{mf}}^{\mathrm{CNPI}}$.

If, in Eq. (5-61), $\boldsymbol{A}$ and $\boldsymbol{B}$ are both invariant subgroups of $\boldsymbol{G}$, then the group product is the *direct product* discussed in connection with Eq. (1-53), and it can be shown that all elements of $\boldsymbol{A}$ commute with all elements of $\boldsymbol{B}$. That is, in the present example we have

$$\boldsymbol{G}_{\mathrm{mf}}^{\mathrm{CNPI}} = \boldsymbol{A} \otimes \boldsymbol{B}. \tag{5-64}$$

The group $\boldsymbol{S}_3$, whose class structure is given in Eq. (5-50), can be written as the product

$$\boldsymbol{S}_3 = \{E, (123), (132)\} \times \{E, (12)\}. \tag{5-65}$$

Comparison with Eq. (5-50) shows that $\{E, (123), (132)\}$ is an invariant subgroup of $\boldsymbol{S}_3$, but that $\{E, (12)\}$ is not. The product given in Eq. (5-65) is called a *semidirect product*. If, in Eq. (5-61), $\boldsymbol{A}$ is an invariant subgroup of $\boldsymbol{G}$, but $\boldsymbol{B}$ is not, we say that $\boldsymbol{G}$ is the semidirect product of $\boldsymbol{A}$ and $\boldsymbol{B}$ and write

$$\boldsymbol{G} = \boldsymbol{A} \circledS \boldsymbol{B}. \tag{5-66}$$

In the present example, we have

$$\boldsymbol{S}_3 = \{E, (123), (132)\} \circledS \{E, (12)\}. \tag{5-67}$$

Semidirect products are discussed further in Appendix 16-1, and used in Section 16.5.2 for developing symmetrized basis functions of the ammonia dimer.

5.8 CHARACTER TABLES

For a given group the characters of the irreducible representations are tabulated in a character table. In a character table the elements in the same class are grouped together, since they all have the same character in each irreducible representation, and only one element in each class is given but the number of elements in each class is indicated. The character table of the $\boldsymbol{S}_3$ group is given in this way in Table 5-2 and the irreducible representations are labeled Γ_1, Γ_2, and Γ_3 following our earlier usage. Groups that are isomorphic to each other have the same character table; the groups $\boldsymbol{S}_3$, $\boldsymbol{D}_3$, $\boldsymbol{C}_{3v}$, and $\boldsymbol{C}_{3v}(\mathrm{M})$ are isomorphic to each other and, therefore, they all have the same character table. The character tables of many MS groups are given in Appendix ***A***. For all groups there is one irreducible representation, such as Γ_1 in $\boldsymbol{S}_3$, that has character +1 for all operations of the group. This representation is called the ***totally symmetric representation*** and is denoted $\Gamma^{(s)}$ in the text; it is variously called A, A_g, A', A_1 etc. in the character tables in Appendix ***A***.

Table 5-2

The character table of the $\boldsymbol{S}_3$ group[a]

$\boldsymbol{S}_3$:	E 1	(12) 3	(123) 2
Γ_1:	1	1	1
Γ_2:	1	−1	1
Γ_3:	2	0	−1

[a] One representative element in each class is given, and the number written below each element is the number of elements in the class.

The character tables of a group can be determined using the following general procedure. Knowing the multiplication table and the class structure of a group it is possible to multiply all the elements in one class C_i by (on the right) all the elements in another class C_j, and it is always so that the resultant elements can be arranged into classes. Let us suppose that the set of elements in the class C_k occurs c_{ijk} times in the product so that we can write

$$C_iC_j = \sum_k c_{ijk}C_k, \tag{5-68}$$

where the sum is over all classes in the group and each C_l means all the elements in that class (note that $c_{ijk} = c_{jik}$). Having determined the coefficients c_{ijk}, the characters can be found from the relation

$$r_ir_j\chi_i\chi_j = \chi[E]\sum_k c_{ijk}r_k\chi_k \tag{5-69}$$

which holds for every representation of the group where r_i is the number of elements in class C_i. The examples given in Chapter 18 should make the application of this technique clear [see, for example, Eqs. (18-16)-(18-23)].

5.8.1 The character tables of MS groups

Using the definition given in Chapter 3 we can set up the MS group for any molecule of interest. To apply the definition we need knowledge of (or we must estimate) the relation of the experimental resolution to the size of each possible tunneling splitting of the energy levels in the molecule. For a rigid nonlinear molecule we have named these MS groups by the name of the appropriate point group followed by (M). For example, the MS group of H_2O in its ground electronic state is called $\boldsymbol{C}_{2v}(\mathrm{M})$. For nonrigid molecules the accepted convention is to name the MS group $\boldsymbol{G}_n$ where n is the order of the group. There can be more than one non-isomorphic group of a given order, and so the $\boldsymbol{G}_n$ notation is not unique. However, this has not caused problems in practice since relatively few of such groups are needed in molecular spectroscopy.

To make use of the MS group we need its character table. For a rigid nonlinear molecule the character table of the MS group is the same as that of the point group, because of their isomorphism, and all these character tables are well known. The sensible consensus has emerged of naming the irreducible representations of these MS groups by the same names as used for the point groups. However, it is important to realize that the MS group and molecular point group are not identical as discussed in Chapter 4. For very many nonrigid molecules the character table of the appropriate MS group $\boldsymbol{G}_n$ has been determined. For a selection of molecules, rigid and nonrigid, the MS group character tables are given in Appendix ***A***. No consensus has emerged for a system of notation to be used for the irreducible representations of MS groups $\boldsymbol{G}_n$, but a unique notation has emerged for most groups. For $\boldsymbol{G}_{16}$ there are two extant notations used for the irreducible representations, and we call them $\Gamma(\mathrm{LH})$ and $\Gamma(\mathrm{MW})$. The $\Gamma(\mathrm{LH})$ notation is that originally proposed by Longuet-Higgins (1963) in his application to the hydrazine molecule. This notation is used for the water dimer by Dyke (1977) and Coudert and Hougen (1988,1990). The $\Gamma(\mathrm{MW})$ notation is that introduced for the ethylene molecule [see Table I of Merer and Watson (1973)], and it is also used by Bunker (1979) for the hydrogen dimer.

5.8.2 The character tables of direct product groups

If a group $\boldsymbol{G}$ is the direct product of two invariant subgroups $\boldsymbol{A}$ and $\boldsymbol{B}$ [see Section 5.7]

$$\boldsymbol{G} = \boldsymbol{A} \otimes \boldsymbol{B}, \tag{5-70}$$

then the irreducible representations of $\boldsymbol{G}$ are obtained in a simple manner from those of $\boldsymbol{A}$ and $\boldsymbol{B}$. The group $\boldsymbol{A}$ has n_A classes and thus n_A irreducible representations $\Gamma_1^{(A)}, \Gamma_2^{(A)}, \Gamma_3^{(A)}, \ldots, \Gamma_{n_A}^{(A)}$; $\boldsymbol{B}$ has n_B classes and thus n_B irreducible representations $\Gamma_1^{(B)}, \Gamma_2^{(B)}, \Gamma_3^{(B)}, \ldots, \Gamma_{n_B}^{(B)}$. Since $\boldsymbol{G}$ is the direct product of $\boldsymbol{A}$ and $\boldsymbol{B}$ we know that all elements of $\boldsymbol{A}$ commute with all elements of $\boldsymbol{B}$. Because of this, we obtain the elements in a class of $\boldsymbol{G}$ by selecting one class from $\boldsymbol{A}$ and one class from $\boldsymbol{B}$, and then combining all the elements in the class from $\boldsymbol{A}$ with all elements in the class from $\boldsymbol{B}$. That is, $\boldsymbol{G}$ has $n_A n_B$ classes and $n_A n_B$ irreducible representations. It is straightforward to show [see Section II.6.8 of Jansen and Boon (1967)] that the irreducible representations of $\boldsymbol{G}$ can be labeled as

$$\Gamma_{ij}^{(G)} = \left(\Gamma_i^{(A)}, \Gamma_j^{(B)}\right), \tag{5-71}$$

where $i = 1, 2, 3, \ldots, n_A$ and $j = 1, 2, 3, \ldots, n_B$. If we denote an arbitrary element of $\boldsymbol{G}$ as $R = R^{(A)}R^{(B)}$, where $R^{(A)}$ is an element of $\boldsymbol{A}$ and $R^{(B)}$ an element of $\boldsymbol{B}$, then the character under R associated with the irreducible representation $\Gamma_{ij}^{(G)}$ of $\boldsymbol{G}$ is given by

$$\chi^{\Gamma_{ij}^{(G)}}[R] = \chi^{\Gamma_i^{(A)}}\left[R^{(A)}\right] \chi^{\Gamma_j^{(B)}}\left[R^{(B)}\right], \tag{5-72}$$

where the characters $\chi^{\Gamma_i^{(A)}}[R^{(A)}]$ and $\chi^{\Gamma_j^{(B)}}[R^{(B)}]$ belong to the irreducible representations $\Gamma_i^{(A)}$ and $\Gamma_j^{(B)}$, respectively. The irreducible representation $\Gamma_{ij}^{(G)}$ is $l_i^{(A)} l_j^{(B)}$-fold degenerate, where $l_i^{(A)}$ is the dimension of $\Gamma_i^{(A)}$ and $l_j^{(B)}$ that of $\Gamma_j^{(B)}$.

If we know the irreducible representations of the groups $\boldsymbol{A}$ and $\boldsymbol{B}$, it is obviously easy to determine the irreducible representations of their direct product $\boldsymbol{G}$ from Eqs. (5-71) and (5-72). As an example we consider the groups $\boldsymbol{C}_s(\mathrm{M})$, $\boldsymbol{C}_{3v}(\mathrm{M})$, and $\boldsymbol{D}_{3h}(\mathrm{M})$, whose character tables are given by Tables A-2, A-6, and A-10, respectively. We have

$$\begin{aligned}\boldsymbol{D}_{3h}(\mathrm{M}) &= \boldsymbol{C}_{3v}(\mathrm{M}) \otimes \boldsymbol{C}_s(\mathrm{M}) \\ &= \{E, (123), (132), (12)^*, (23)^*, (13)^*\} \otimes \{E, E^*\}.\end{aligned} \tag{5-73}$$

Comparison of Tables A-2, A-6, and A-10 shows that the irreducible representations of $\boldsymbol{D}_{3h}(\mathrm{M})$ are related to those of $\boldsymbol{C}_{3v}(\mathrm{M})$ and $\boldsymbol{C}_s(\mathrm{M})$ as [Eq. (5-71)]: $A_1' = (A_1, A')$, $A_1'' = (A_2, A'')$, $A_2' = (A_2, A')$, $A_2'' = (A_1, A'')$, $E' = (E, A')$, and $E'' = (E, A'')$.

5.9 CORRELATION TABLES

The correlation rule, as it applies to showing how the irreducible representations of a group correlate to those of a subgroup, is well known and easy to understand. Suppose we have labeled the energy levels[1] of a molecule using the irreducible representation labels of the CNPI group $\boldsymbol{G}$ and that we wish to label them in the MS group $\boldsymbol{H}$ which is a subgroup of $\boldsymbol{G}$. The symmetry labels obtained using the irreducible representations of $\boldsymbol{H}$, can be deduced from those of $\boldsymbol{G}$ once the correlation of the irreducible representations of $\boldsymbol{G}$ to those of $\boldsymbol{H}$ is known.

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[1] The idea of labeling molecular energy levels using irreducible representations of a symmetry group is introduced in the preamble to Chapter 3.

To appreciate how this correlation is determined let us consider that the group $\boldsymbol{G}$, of order g, has elements $\{G_1, G_2, \ldots, G_g\}$ and that its subgroup $\boldsymbol{H}$ of order $h < g$, has elements $\{H_1, H_2, \ldots, H_h\}$. Further suppose that $H_1 = G_1, H_2 = G_2, \ldots, H_h = G_h$. Any irreducible matrix representation, Γ_α, say, of $\boldsymbol{G}$ will provide a matrix representation of $\boldsymbol{H}$ by considering only the matrices corresponding to the elements $G_1, G_2, \ldots, G_h$ of $\boldsymbol{G}$. This matrix representation of $\boldsymbol{H}$ will in general be reducible and the irreducible representation, Γ_i, say, of $\boldsymbol{H}$ will occur $a_i^{(\alpha)}$ times where [from Eq. (5-45)]

$$a_i^{(\alpha)} = \frac{1}{h}\sum_{r=1}^{h} \chi^{\Gamma_\alpha}[H_r]\chi^{\Gamma_i}[H_r]^*, \tag{5-74}$$

and $\chi^{\Gamma_\alpha}[H_r]$ and $\chi^{\Gamma_i}[H_r]$ are the characters in the representations Γ_α and Γ_i for the operation $H_r = G_r$. We can represent this reduction by writing

$$\Gamma_\alpha = a_1^{(\alpha)}\Gamma_1 \oplus a_2^{(\alpha)}\Gamma_2 \oplus \cdots = \sum_i a_i^{(\alpha)}\Gamma_i. \tag{5-75}$$

Equation (5-75) shows how the irreducible representation Γ_α of $\boldsymbol{G}$ correlates with the irreducible representations (Γ_i) of $\boldsymbol{H}$; if a molecular wavefunction transforms as Γ_α in $\boldsymbol{G}$ it will transform as the right hand side of Eq. (5-75) in $\boldsymbol{H}$, where the $a_i^{(\alpha)}$ are obtained from Eq. (5-74).

As an example of this let us consider the correlation of the irreducible representations of the CNPI group of ethylene $\boldsymbol{G}_{96}$, where

$$\boldsymbol{G}_{96} = \boldsymbol{S}_4^{(\mathrm{H})} \otimes \boldsymbol{S}_2^{(\mathrm{C})} \otimes \boldsymbol{\mathcal{E}}, \tag{5-76}$$

with the irreducible representations of the MS group $\boldsymbol{D}_{2\mathrm{h}}(\mathrm{M})$ of a rigidly planar ethylene molecule in the configuration at the top of the character table for the group $\boldsymbol{D}_{2\mathrm{h}}(\mathrm{M})$ given in Table A-9. The character tables of the groups $\boldsymbol{S}_4^{(\mathrm{H})}$, $\boldsymbol{S}_2^{(\mathrm{C})}$, and $\mathcal{E}$ are given in Table 5-3 and the character table of $\boldsymbol{G}_{96}$ can be deduced from these by multiplication (see Section 5.8.2). The 20 irreducible representations of $\boldsymbol{G}_{96}$ are labeled $\Gamma_\alpha{}^\beta$ where $\Gamma = A, B, E, F$, or G according to the character of the representation under the elements of $\boldsymbol{S}_4^{(\mathrm{H})}$, α = s or a as the character is positive or negative under (56), and $\beta = +$ or $-$ as the character under E^* is positive or negative. The correlation of the irreducible representations of $\boldsymbol{G}_{96}$ with those of the $\boldsymbol{D}_{2\mathrm{h}}(\mathrm{M})$ group can be obtained by using Eqs. (5-74) and (5-75) and the correlation table is given in Table 5-4.

Table 5-3

The groups $S_4^{(H)}$, $S_2^{(C)}$ and $\mathcal{E}$ for ethylene[a]

$S_4^{(H)}$:	E	(12)	(12)(34)	(123)	(1234)
	1	6	3	8	6
A:	1	1	1	1	1
B:	1	−1	1	1	−1
E:	2	0	2	−1	0
F:	3	1	−1	0	−1
G:	3	−1	−1	0	1

$S_2^{(C)}$:	E	(56)
s:	1	1
a:	1	−1

$\mathcal{E}$:	E	E^*
+:	1	1
−:	1	−1

[a] Here the CNPI group G_{96} is given by $S_4^{(H)} \otimes S_2^{(C)} \otimes \mathcal{E}$.

Examples of the results of using Eq. (5-74) are

$$a_{B_{1u}}^{(F_s^+)} = a_{B_{3g}}^{(F_s^+)} = a_{B_{2u}}^{(F_s^+)} = 1, \tag{5-77}$$

with all other $a_i^{(F_s^+)} = 0$, and

$$a_{A_u}^{(E_s^-)} = 2, \tag{5-78}$$

with all other $a_i^{(E_s^-)} = 0$. From these equations we can use Eq. (5-75) to obtain

$$F_s^+ = B_{1u} \oplus B_{2u} \oplus B_{3g} \tag{5-79}$$

and

$$E_s^- = 2A_u. \tag{5-80}$$

Table 5-4

Correlation table for the CNPI group of ethylene (G_{96}) to the MS group D_{2h}(M)

G_{96}	D_{2h}(M)	G_{96}	D_{2h}(M)
A_s^+	A_g	A_s^-	A_u
B_s^+	A_g	B_s^-	A_u
E_s^+	$2A_g$	E_s^-	$2A_u$
F_s^+	$B_{1u} \oplus B_{2u} \oplus B_{3g}$	F_s^-	$B_{1g} \oplus B_{2g} \oplus B_{3u}$
G_s^+	$B_{1u} \oplus B_{2u} \oplus B_{3g}$	G_s^-	$B_{1g} \oplus B_{2g} \oplus B_{3u}$
A_a^+	B_{1u}	A_a^-	B_{1g}
B_a^+	B_{1u}	B_a^-	B_{1g}
E_a^+	$2B_{1u}$	E_a^-	$2B_{1g}$
F_a^+	$A_g \oplus B_{2u} \oplus B_{3g}$	F_a^-	$A_u \oplus B_{2g} \oplus B_{3u}$
G_a^+	$A_g \oplus B_{2u} \oplus B_{3g}$	G_a^-	$A_u \oplus B_{2g} \oplus B_{3u}$

Problem 5-4. Determine the correlation table of the CNPI group of NF_3, given in Eq. (3-6), with the MS group of the molecule, given in Eq. (3-9). These groups are called $\boldsymbol{D}_{3h}$(M) and $\boldsymbol{C}_{3v}$(M), respectively, and their character tables are given in Tables A-6 and A-10 (see also Section 5.8.2).

Answer. The group $\boldsymbol{D}_{3h}$(M) has six irreducible representations, A_1', A_2', E', A_1'', A_2'', and E'', and the group $\boldsymbol{C}_{3v}$(M) has three, A_1, A_2, and E. The representation A_1' of $\boldsymbol{D}_{3h}$(M) has character +1 under each operation and hence correlates with the representation A_1 of $\boldsymbol{C}_{3v}$(M). Similarly A_2'' of $\boldsymbol{D}_{3h}$(M) has character +1 under the operations E, (123), (132), $(12)^*$, $(23)^*$, and $(13)^*$ so that it correlates with A_1 of $\boldsymbol{C}_{3v}(M)$. The representations A_2' and A_1'' each have characters $1, 1, 1, -1, -1$, and -1 under the operations E, (123), (132), $(12)^*$, $(23)^*$, and $(13)^*$, respectively, and so each correlates with the representation A_2 of $\boldsymbol{C}_{3v}$(M). Finally E' and E'' of $\boldsymbol{D}_{3h}$(M) each have characters 2, -1, -1, 0, 0, and 0 under E, (123), (132), $(12)^*$, $(23)^*$, and $(13)^*$, respectively. and so each correlates with the representation E of $\boldsymbol{C}_{3v}$(M). Thus, for example, a pair of functions transforming as E' or E'' in $\boldsymbol{D}_{3h}$(M) transform as E in $\boldsymbol{C}_{3v}$(M).

5.9.1 Reverse correlation tables and induced representations

We can equally well discuss the correlation of the irreducible representations in the other direction, i.e., from the MS group $\boldsymbol{H}$ to the CNPI group $\boldsymbol{G}$, and this is useful when we want to consider the effect of small tunneling splittings. Suppose we have symmetry labeled a level as Γ_i in $\boldsymbol{H}$. We wish to know what the symmetry of the level would be if all tunneling splittings were allowed for and the CNPI group $\boldsymbol{G}$ used. It has been shown by Watson (1965) that the symmetry in $\boldsymbol{G}$, which we call $\Gamma(\Gamma_i)$ is given by

$$\Gamma(\Gamma_i) = \sum_\alpha a_i^{(\alpha)}\Gamma_\alpha \tag{5-81}$$

in terms of the irreducible representations Γ_α of $\boldsymbol{G}$, where the $a_i^{(\alpha)}$ are as given in Eq. (5-74). The representation $\Gamma(\Gamma_i)$ is the representation of $\boldsymbol{G}$ *induced* by the representation Γ_i of the subgroup $\boldsymbol{H}$. Thus given the symmetry species of a level in the group $\boldsymbol{H}$ and the correlation table relating the irreducible representations of $\boldsymbol{G}$ to $\boldsymbol{H}$, we can use the correlation table *backwards* to determine the symmetries of the levels in the larger group $\boldsymbol{G}$.

We can use the correlation table of the $\boldsymbol{D}_{2h}(M)$ and $\boldsymbol{G}_{96}$ groups of ethylene as an example. For ethylene the rotation-vibration levels of the ground electronic state can be labeled using the eight irreducible representation labels of the $\boldsymbol{D}_{2h}(M)$ group since there are no tunneling splittings. If we wished to use the $\boldsymbol{G}_{96}$ group to classify the levels then the species of each level could be obtained from the species in $\boldsymbol{D}_{2h}(M)$ by using Table 5-4 backwards. For example, a level of species A_u in $\boldsymbol{D}_{2h}(M)$ will have species $\Gamma(A_u)$ in $\boldsymbol{G}_{96}$ where

$$\Gamma(A_u) = \sum_\alpha a_{Au}^{(\alpha)}\Gamma_\alpha \tag{5-82}$$

and Γ_α are the irreducible representations of $\boldsymbol{G}_{96}$. From Table 5-4 we have

$$a_{A_u}^{(E_s^-)} = 2, \quad a_{A_u}^{(A_s^-)} = a_{A_u}^{(B_s^-)} = a_{A_u}^{(F_a^-)} = a_{A_u}^{(G_a^-)} = 1, \tag{5-83}$$

and all other $a_{Au}^{(\alpha)}$ are zero. Thus

$$\Gamma(A_u) = A_s^- \oplus B_s^- \oplus 2E_s^- \oplus F_a^- \oplus G_a^- . \tag{5-84}$$

To obtain the representation in $\boldsymbol{G}_{96}$ induced by the irreducible representations of $\boldsymbol{D}_{2h}(M)$ we use the normal correlation table backwards and the *reverse correlation table* obtained for $\boldsymbol{D}_{2h}(M) \rightarrow \boldsymbol{G}_{96}$ is given in Table 5-5.

Table 5-5

Reverse correlation table for $\boldsymbol{D}_{2h}(M)$ to the CNPI group of ethylene ($\boldsymbol{G}_{96}$)

$\boldsymbol{D}_{2h}(M)$	$\boldsymbol{G}_{96}$	$\boldsymbol{D}_{2h}(M)$	$\boldsymbol{G}_{96}$
A_g	$A_s^+ \oplus B_s^+ \oplus 2E_s^+ \oplus F_a^+ \oplus G_a^+$	A_u	$A_s^- \oplus B_s^- \oplus 2E_s^- \oplus F_a^- \oplus G_a^-$
B_{1g}	$A_a^- \oplus B_a^- \oplus 2E_a^- \oplus F_s^- \oplus G_s^-$	B_{1u}	$A_a^+ \oplus B_a^+ \oplus 2E_a^+ \oplus F_s^+ \oplus G_s^+$
B_{2g}	$F_s^- \oplus G_s^- \oplus F_a^- \oplus G_a^-$	B_{2u}	$F_s^+ \oplus G_s^+ \oplus F_a^+ \oplus G_a^+$
B_{3g}	$F_s^+ \oplus G_s^+ \oplus F_a^+ \oplus G_a^+$	B_{3u}	$F_s^- \oplus G_s^- \oplus F_a^- \oplus G_a^-$

We are now in a position to appreciate the utility of the MS group. In the ethylene molecule no tunneling splittings are observed in the ground electronic state energy levels, and the MS group is $\boldsymbol{D}_{2h}(M)$. Using this group the rotation-vibration energy levels are labeled according to the irreducible representation labels A_g, A_u, B_{1g}, etc. If we used the CNPI group $\boldsymbol{G}_{96}$ to label the levels then a level labeled A_g in $D_{2h}(M)$ would be labeled $(A_s{}^+ \oplus B_s{}^+ \oplus 2E_s{}^+ \oplus F_a{}^+ \oplus G_a{}^+)$, and so on according to Table 5-5 for each of the eight possible irreducible representation labels of $\boldsymbol{D}_{2h}(M)$. We see that according to the CNPI group classification each nondegenerate level of ethylene [in $\boldsymbol{D}_{2h}(M)$] is twelvefold degenerate and there is a lot of "accidental" degeneracy. Since no tunneling splittings are observed we have no use for the symmetry labels of the individual split levels, and a classification that distinguishes between the eight possible symmetry types without allowing for the splitting is enough. This is what the MS group, $\boldsymbol{D}_{2h}(M)$ in this case, provides. Notice from Table 5-5 that the twelvefold structural degeneracy is not completely resolvable by tunneling; the A_g, B_{1g}, A_u, and B_{1u} levels in $\boldsymbol{D}_{2h}(M)$ can only at most be split into six levels by tunneling and the B_{2g}, B_{3g}, B_{2g}, and B_{3u} levels into four. In an excited electronic state of ethylene it may be that torsional tunneling is observable, in which case the MS group would be the group $\boldsymbol{G}_{16}$ (see Table A-25). Part of the structural degeneracy would then be allowed for in the symmetry classification but not all of it; only that part capable of experimental resolution.

Problem 5-5. Using the $\boldsymbol{D}_{2h}(M)$ group (see Table A-9) there are eight symmetry types for the rotation-vibration levels of nontunneling planar ethylene. Determine the successive correlations of these species to the species of the groups $\boldsymbol{G}_{16}$ (see Table A-25) and $\boldsymbol{G}_{96}$ by using the correlation tables of $\boldsymbol{G}_{16}$ to $\boldsymbol{D}_{2h}(M)$ and of $\boldsymbol{G}_{96}$ to $\boldsymbol{G}_{16}$. The $\boldsymbol{G}_{16}$ group allows for torsional tunneling, and we use the $\Gamma(MW)$ notation for its irreducible representations.

Answer. To determine the reverse correlation $\boldsymbol{D}_{2h}(M) \rightarrow \boldsymbol{G}_{16}$ we must first determine the correlation $\boldsymbol{G}_{16} \rightarrow \boldsymbol{D}_{2h}(M)$. Using the character tables in Tables A-9 and A-25 this is straightforward, and the correlation table obtained is given in the left hand half of Table 5-6. The reverse correlation table, obtained by using the correlation table backwards according to Eq. (5-81), is given in the right hand half of Table 5-6. We see that levels of symmetry B_{2g}, B_{3g}, B_{2u}, and B_{3u} cannot be split by torsional tunneling. The correlation table and reverse correlation table for $\boldsymbol{G}_{96} \rightarrow \boldsymbol{G}_{16}$ is given in Table 5-7; the plus and minus signs correlate unchanged since E^* is present in both groups. These reverse correlation tables can be combined to show the successive reverse correlations $\boldsymbol{D}_{2h}(M) \rightarrow \boldsymbol{G}_{16} \rightarrow \boldsymbol{G}_{96}$. For example, a level of A_g symmetry in $\boldsymbol{D}_{2h}(M)$ correlates with $\boldsymbol{G}_{16}$ and $\boldsymbol{G}_{96}$ species as follows:

$$A_g \rightarrow \begin{cases} A_1{}^+ & \rightarrow A_s{}^+ \oplus E_s{}^+ \oplus F_a{}^+ \\ B_1{}^+ & \rightarrow B_s{}^+ \oplus E_s{}^+ \oplus G_a{}^+. \end{cases} \qquad (5\text{-}85)$$

Such a connected reverse correlation would be useful if one were interested in the effect of successive tunnelings. The reader can easily construct a similar reverse correlation table for $\boldsymbol{C}_2(\mathrm{M}) \rightarrow \boldsymbol{G}_4 \rightarrow \boldsymbol{G}_8$ for the H_2O_2 molecule (see Tables A-4, A-21, A-23, and B-4(v)).

Table 5-6

Correlation and reverse correlation tables for the $\boldsymbol{D}_{2\mathrm{h}}(\mathrm{M})$ and $\boldsymbol{G}_{16}$ groups of ethylene[a]

$\boldsymbol{G}_{16}$	$\boldsymbol{D}_{2\mathrm{h}}(\mathrm{M})$	$\boldsymbol{D}_{2\mathrm{h}}(\mathrm{M})$	$\boldsymbol{G}_{16}$
A_1^+	A_g	A_g	$A_1^+ \oplus B_1^+$
A_2^+	B_{1u}	B_{1g}	$A_2^- \oplus B_2^-$
B_1^+	A_g	B_{2g}	E^-
B_2^+	B_{1u}	B_{3g}	E^+
E^+	$B_{2u} \oplus B_{3g}$		
		A_u	$A_1^- \oplus B_1^-$
A_1^-	A_u	B_{1u}	$A_2^+ \oplus B_2^+$
A_2^-	B_{1g}	B_{2u}	E^+
B_1^-	A_u	B_{3u}	E^-
B_2^-	B_{1g}		
E^-	$B_{2g} \oplus B_{3u}$		

[a] We use the $\Gamma(\mathrm{MW})$ notation for the irreducible representations of $\boldsymbol{G}_{16}$.

Table 5-7

Correlation and reverse correlation tables for the $\boldsymbol{G}_{16}$ and $\boldsymbol{G}_{96}$ groups of ethylene[a]

$\boldsymbol{G}_{96}$	$\boldsymbol{G}_{16}$	$\boldsymbol{G}_{16}$	$\boldsymbol{G}_{96}$
$A_s^\pm$	$A_1^\pm$	$A_1^\pm$	$A_s^\pm \oplus E_s^\pm \oplus F_a^\pm$
$B_s^\pm$	$B_1^\pm$	$A_2^\pm$	$B_a^\pm \oplus E_a^\pm \oplus G_s^\pm$
$E_s^\pm$	$A_1^\pm \oplus B_1^\pm$	$B_1^\pm$	$B_s^\pm \oplus E_s^\pm \oplus G_a^\pm$
$F_s^\pm$	$B_2^\pm \oplus E^\pm$	$B_2^\pm$	$A_a^\pm \oplus E_a^\pm \oplus F_s^\pm$
$G_s^\pm$	$A_2^\pm \oplus E^\pm$	$E^\pm$	$F_s^\pm \oplus G_s^\pm \oplus F_a^\pm \oplus G_a^\pm$
$A_a^\pm$	$B_2^\pm$		
$B_a^\pm$	$A_2^\pm$		
$E_a^\pm$	$A_2^\pm \oplus B_2^\pm$		
$F_a^\pm$	$A_1^\pm \oplus E^\pm$		
$G_a^\pm$	$B_1^\pm \oplus E^\pm$		

[a] We use the $\Gamma(\mathrm{MW})$ notation for the irreducible representations of $\boldsymbol{G}_{16}$.

Such connected reverse correlation tables are particularly useful for weakly bound cluster molecules. This is because in such molecules several different degenerate rearrangements can or cannot be feasible, and as a result several different MS groups have to be considered. As an example we consider the water dimer that was discussed in Chapter 3. For the water dimer we consider three different MS groups: $\boldsymbol{C}_s(\mathrm{M}) = \{E, (34)^*\}$, $\boldsymbol{G}_4 = \{E, (34), E^*, (34)^*\}$, and $\boldsymbol{G}_{16}$ given in Eq. (3-23). The MS group $\boldsymbol{C}_s$ is appropriate for version (1) of the water dimer given in Fig. 3-15 if no degenerate rearrangements are feasible (i.e., if it is a rigid molecule). The MS group $\boldsymbol{G}_4$ is appropriate if only the acceptor tunneling degenerate rearrangement is feasible [which interconverts versions (1) and (4) in Fig. 3-15], and $\boldsymbol{G}_{16}$ is the MS group if both the acceptor tunneling and donor-acceptor interchange tunneling are feasible (in which case all eight versions in Fig. 3-15 are accessible to each other). The character tables are given in Table A-2 [with $(34)^*$ replacing E^*] for the $\boldsymbol{C}_s$ group, in Table A-21 [with (34) replacing (12)(34), and $(34)^*$ replacing $(12)(34)^*$] for the $\boldsymbol{G}_4$ group, and in Table A-25 for the $\boldsymbol{G}_{16}$ group. The reverse correlations are [where we use the $\Gamma(\mathrm{LH})$ notation for the irreducible representations of the $\boldsymbol{G}_{16}$ group and the Γ_3 notation for the group $\boldsymbol{G}_4$]

$$A' \rightarrow \begin{cases} B_1 & \rightarrow A_2{}^- \oplus B_2{}^- \oplus E^- \\ A_1 & \rightarrow A_1{}^+ \oplus B_1{}^+ \oplus E^+, \end{cases} \tag{5-86}$$

$$A'' \rightarrow \begin{cases} B_2 & \rightarrow A_2{}^+ \oplus B_2{}^+ \oplus E^+ \\ A_2 & \rightarrow A_1{}^- \oplus B_1{}^- \oplus E^-. \end{cases} \tag{5-87}$$

It is left as an exercise for the reader to determine the reverse correlations $\boldsymbol{C}_s(\mathrm{M}) \rightarrow \boldsymbol{C}_{6v}(\mathrm{M}) \rightarrow \boldsymbol{G}_{24} \rightarrow \boldsymbol{G}_{24} \otimes \mathcal{E}$ for the benzene-water dimer [see Eqs. (3-24)-(3-26); the character table of the $\boldsymbol{C}_{6v}(\mathrm{M})$ group is given in Table A-7, and the character table of the $\boldsymbol{G}_{24}$ group is given in Table A-27]. In doing this the simplification occurring when direct product groups appear in this manner in the chain will be realized.[2]

BIBLIOGRAPHICAL NOTES

Matrices

Margenau and Murphy (1956). In Chapter 10 matrices and matrix algebra are discussed.

Representation theory

Hamermesh (1964). Chapter 7 discusses permutation groups and their representations.

Murnaghan (1938). Equations (5-68) and (5-69) in this chapter are proved on page 83.

Tinkham (1964). Representations are discussed in Chapter 3.

Wigner (1959). The orthogonality relation [Eq. (5-40) in this chapter] is proved and discussed in Chapter 9 [see Eq.(9.32)], and the proof that any matrix representation can be transformed into a unitary matrix representation is given in Eqs. (9.4)-(9.7). Equation (5-47) of this chapter is proved on page 115 of Wigner's book, and the equality of the number of classes in a group to the number of irreducible representations of the group is discussed on page 84.

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[2] After having determined the reverse correlations see Eqs. (8-47) and (8-48).

The determination of character tables

Stone (1964). The use of basis functions to generate the irreducible representations of a 'new' MS group is discussed.

Dixon (1967). This paper proposes a practical procedure, based on Eq. (5-69), for computing the characters of the irreducible representations for finite groups (of order up to approximately 1000). This procedure has later become known as *Dixon's Character Table Algorithm.*

Schneider (1990). A more efficient version of Dixon's Character Table Algorithm is described.

Blokker (1972, 1973), Flodmark and Jansson (1982), and Lee and Chen (1986). These authors propose algorithms related to Dixon's Character Table Algorithm. The new algorithms, however, calculate not only the characters of the irreducible representations, but also sets of representation matrices associated with them.

Woodman (1970). The use of the product decomposition of an MS group to subgroups is discussed [see Section 5.7]. Woodman shows that when a large MS group can be expressed as a direct or semidirect product of smaller subgroups, one need only classify the molecular wavefunctions in the subgroups and one can avoid the tedious construction of the character table of the MS group. In Section 16.5.2 we explain how the product decomposition of the MS group of the ammonia dimer, $\boldsymbol{G}_{144}$, is used to obtain symmetrized basis functions.

Balasubramanian (1980). Generalized wreath product groups are discussed and application to some MS groups is made. A wreath product is a particular type of semidirect product (Section 5.7).

Odutola, Alvis, Curtis, and Dyke (1981), and Odutola and Adekola (1987). Product decomposition is used to analyze the permutation-inversion groups of weakly bound cluster molecules. The former paper considers dimers, and the latter paper considers trimers and higher polymers in particular the ammonia trimer and tetramer as well as the benzene trimer.

Lehmann and Pate (1990). The character table of the MS group $\boldsymbol{G}_{162}$ of the molecule $(CH_3)_3CCCH$ is derived allowing for internal rotation of the methyl groups. An interesting feature of this group is that all the permutations are even.

Soldán (1996, 1997). Product decomposition is used to analyze the permutation-inversion groups for molecules with two coaxial rotors, including the extended molecular symmetry groups discussed in Chapters 15 and 17.

6

The Symmetry Labeling of Molecular Energy Levels

An approximate time independent Schrödinger equation for a molecule is introduced, and the effect of a nuclear permutation and the inversion E^* on this equation is discussed. Symmetry operations and symmetry groups are defined with respect to this Hamiltonian, and it is shown how molecular wavefunctions, and products of them, generate representations of a symmetry group of the Hamiltonian. As a result we can label energy levels with representation labels and use these labels to distinguish energy levels. The general use of these labels in determining which pairs of levels can interact with each other in certain circumstances is discussed, and the vanishing integral rule is derived.

6.1 A MOLECULAR SCHRÖDINGER EQUATION IN (X, Y, Z) COORDINATES

With some simplifying approximations we can write the classical nonrelativistic energy of a molecule in free space as the sum of the kinetic energies of the nuclei and electrons and of the electrostatic interactions between them. Neglecting the translational motion of the molecule and expressing the energy in terms of the coordinates and momenta (rather than in terms of the coordinates and velocities) we obtain this approximate classical energy in *Hamiltonian form* H^0; using the (X, Y, Z) coordinate system (with origin at the molecular center of mass) we have:[1]

$$H^0 = \frac{1}{2}\sum_r \frac{\boldsymbol{P}_r{}^2}{m_r} + \sum_{r<s} \frac{C_r C_s e^2}{4\pi\epsilon_0 R_{rs}}, \tag{6-1}$$

where r, s run over all the nuclei and electrons in the molecule, particle r has mass m_r and charge $C_r e$ (the mass of an electron is m_e and its charge is $-e$), and the momentum of particle r is $\boldsymbol{P}_r$; we can write

$$\boldsymbol{P}_r{}^2 = m_r{}^2(\dot{X}_r{}^2 + \dot{Y}_r{}^2 + \dot{Z}_r{}^2) = P_{X_r}^2 + P_{Y_r}^2 + P_{Z_r}^2, \tag{6-2}$$

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[1] The factor $4\pi\epsilon_0$ (where ϵ_0 is the permittivity of vacuum) occurs in the denominator of the potential energy so that this expression is in SI units; see Eq. (12) in Section 7.3 of Mills, Cvitaš, Homann, Kallay, and Kuchitsu (1993).

where $\dot{X}_r = dX_r/dt$ and t is time. In Eq. (6-1) the distance between the particles r and s is written R_{rs} and

$$R_{rs} = [(X_r - X_s)^2 + (Y_r - Y_s)^2 + (Z_r - Z_s)^2]^{1/2}. \tag{6-3}$$

In Eq. (6-1) we use C_re for the charge rather than the more customary Z_re to avoid confusion with the coordinate Z_r.

From the basic postulates of quantum mechanics the allowed stationary state energies of a molecule with classical energy given by Eq. (6-1) are the *eigenvalues* E_n in the time independent Schrödinger equation

$$\hat{H}^0\Psi_n = E_n\Psi_n, \tag{6-4}$$

where the *eigenfunctions* Ψ_n are single valued functions of the coordinates of the nuclei and electrons in the molecule, and the quantum mechanical *Hamiltonian operator* [or simply *Hamiltonian*] $\hat{H}^0$ is obtained from H^0 in Eq. (6-1) by replacing the Cartesian momenta P_{X_r}, etc., by the operators $\hat{P}_{X_r}$, etc., according to the prescription

$$\hat{P}_{X_r} = -i\hbar\partial/\partial X_r, \quad \text{etc.}, \tag{6-5}$$

where $\hbar = h/2\pi$ and h is Planck's constant. We obtain

$$\hat{H}^0 = -\frac{\hbar^2}{2}\sum_r \frac{\nabla_r{}^2}{m_r} + \sum_{r<s} \frac{C_rC_se^2}{4\pi\epsilon_0 R_{rs}}, \tag{6-6}$$

where

$$\nabla_r{}^2 = (\partial^2/\partial X_r{}^2 + \partial^2/\partial Y_r{}^2 + \partial^2/\partial Z_r{}^2). \tag{6-7}$$

The effect of the electron spin magnetic moment, and of the possible magnetic and electric moments of each nucleus, will be to add further electric and magnetic interaction terms to the energy in Eq. (6-1) and hence to the Hamiltonian operator in Eq. (6-6). Even without worrying about these terms the use of an axis system with origin at the molecular center of mass leads to a slightly more complicated Hamiltonian than $\hat{H}^0$ after we discard the translational energy, and this is discussed in Chapter 7. For the general arguments we wish to make in this chapter we neglect all these extra terms. Equation (6-6) is an approximate molecular Hamiltonian operator, and in this chapter we use representation theory to label the energy levels (eigenstates) of this particular approximate Hamiltonian in order to show how the process of labeling energy levels works.

6.2 THE EFFECTS OF NUCLEAR PERMUTATIONS AND THE INVERSION ON THE SCHRÖDINGER EQUATION

We will consider the Schrödinger equation, Eq. (6-4), for a molecule in which nuclei 1 and 2 are identical, having mass m and charge Ce. In these circumstances we can write the Hamiltonian operator of Eq. (6-6) as

$$\hat{H}^0 = \hat{H}^0(1,2) + \hat{H}^0(\text{rest}), \tag{6-8}$$

where

$$\hat{H}^0(1,2) = -\frac{\hbar^2}{2m}(\nabla_1{}^2 + \nabla_2{}^2) + \frac{C^2e^2}{4\pi\epsilon_0 R_{12}} + \sum_{r\neq 1,2} \frac{CC_re^2}{4\pi\epsilon_0}\left(\frac{1}{R_{1r}} + \frac{1}{R_{2r}}\right). \tag{6-9}$$

$\hat{H}^0$ (rest), therefore, does not involve the coordinates or momenta of nuclei 1 and 2. The Schrödinger equation, Eq. (6-4), for the molecule is

$$\begin{aligned}[\hat{H}^0(1,2) + \hat{H}^0(\text{rest})]\Psi_n(X_1,Y_1,Z_1,X_2,Y_2,Z_2,W)\\ = E_n\Psi_n(X_1,Y_1,Z_1,X_2,Y_2,Z_2,W),\end{aligned} \tag{6-10}$$

where W stands for the coordinates of all the other nuclei and of all the electrons in the molecule.

We wish to examine the effect of permuting nuclei 1 and 2, i.e., the effect of the operation (12), on the Schrödinger equation given in Eq. (6-10). The effect of (12) on the right hand side of the Schrödinger equation can be written

$$\begin{aligned}&(12)E_n\Psi_n(X_1,Y_1,Z_1,X_2,Y_2,Z_2,W)\\ &\quad = E_n(12)\Psi_n(X_1,Y_1,Z_1,X_2,Y_2,Z_2,W) && \text{(6-11)}\\ &\quad = E_n\Psi_n(X_2,Y_2,Z_2,X_1,Y_1,Z_1,W) && \text{(6-12)}\\ &\quad = E_n\Psi_n^{(12)}(X_1,Y_1,Z_1,X_2,Y_2,Z_2,W). && \text{(6-13)}\end{aligned}$$

Equation (6-11) simply results from the fact that E_n is a constant, independent of the coordinates of nuclei 1 and 2, and hence unaffected by (12). Equation (6-12) shows the effect of (12) on Ψ_n and the value of the function at the point (X_1, Y_1, Z_1, X_2, Y_2, Z_2, W) in configuration space is changed to its value at the point (X_2, Y_2, Z_2, X_1, Y_1, Z_1, W). Equation (6-13) introduces $\Psi_n^{(12)}$ as a new function whose value at the point (X_1, Y_1, Z_1, X_2, Y_2, Z_2, W) is the same as the value of Ψ_n at the point (X_2, Y_2, Z_2, X_1, Y_1, Z_1, W) [see Section 1.1.1].

The effect of (12) on the left hand side of Eq. (6-10) can be written

$$\begin{aligned}&(12)\left\{-\frac{\hbar^2}{2m}(\nabla_1{}^2 + \nabla_2{}^2) + \frac{C^2e^2}{4\pi\epsilon_0 R_{12}} + \sum_{r\neq 1,2} \frac{CC_re^2}{4\pi\epsilon_0}\left(\frac{1}{R_{1r}} + \frac{1}{R_{2r}}\right)\right.\\ &\qquad\left. + \hat{H}^0(\text{rest})\right\}\Psi_n(X_1,Y_1,Z_1,X_2,Y_2,Z_2,W)\\ &= \left\{-\frac{\hbar^2}{2m}(\nabla_2{}^2 + \nabla_1{}^2) + \frac{C^2e^2}{4\pi\epsilon_0 R_{21}} + \sum_{r\neq 1,2} \frac{CC_re^2}{4\pi\epsilon_0}\left(\frac{1}{R_{2r}} + \frac{1}{R_{1r}}\right)\right.\\ &\qquad\left. + \hat{H}^0(\text{rest})\right\}(12)\Psi_n(X_1,Y_1,Z_1,X_2,Y_2,Z_2,W),\end{aligned} \tag{6-14}$$

that is,

$$\begin{aligned}&(12)[\hat{H}^0(1,2) + \hat{H}^0(\text{rest})]\Psi_n(X_1,Y_1,Z_1,X_2,Y_2,Z_2,W)\\ &\quad = [\hat{H}^0(2,1) + \hat{H}^0(\text{rest})](12)\Psi_n(X_1,Y_1,Z_1,X_2,Y_2,Z_2,W).\end{aligned} \tag{6-15}$$

Since nuclei 1 and 2 have the same mass and charge $H^0(2,1)$ is identical to $H^0(1,2)$, and we can write

$$\begin{aligned}(12)[H^0(1,2) + H^0(\text{rest})]\Psi_n(X_1, Y_1, Z_1, X_2, Y_2, Z_2, W) \\ = [H^0(1,2) + H^0(\text{rest})](12)\Psi_n(X_1, Y_1, Z_1, X_2, Y_2, Z_2, W).\end{aligned} \tag{6-16}$$

The right hand side of Eq. (6-16) becomes

$$\begin{aligned}[H^0(1,2) + H^0(\text{rest})]\Psi_n(X_2, Y_2, Z_2, X_1, Y_1, Z_1, W) \\ = [H^0(1,2) + H^0(\text{rest})]\Psi_n^{(12)}(X_1, Y_1, Z_1, X_2, Y_2, Z_2, W).\end{aligned} \tag{6-17}$$

Equation (6-16) shows that the effect of $(12)H^0$ on any function Ψ_n is the same as the effect of $H^0(12)$ when 1 and 2 are identical. Thus the operation (12) commutes with this particular Hamiltonian operator H^0 and we can write the operator equation

$$(12)H^0 = H^0(12). \tag{6-18}$$

In general the molecular Hamiltonian operator given in Eq. (6-6) will commute with any operation that is a permutation of identical nuclei (and similarly with any permutation of the electrons). As a direct result of Eq. (6-18) we have [by equating the right hand side of Eq. (6-17) with Eq. (6-13)]

$$H^0\Psi_n^{(12)}(X_1, Y_1, Z_1, X_2, Y_2, Z_2, W) = E_n\Psi_n^{(12)}(X_1, Y_1, Z_1, X_2, Y_2, Z_2, W), \tag{6-19}$$

and the operation (12) has converted Ψ_n to a new function $\Psi_n^{(12)}$ which is also an eigenfunction of H^0 with eigenvalue E_n. In general we can say that any operation R that commutes with the molecular Hamiltonian will convert an eigenfunction of the Hamiltonian to a new function having the same eigenvalue and such an operation is called a ***symmetry operation*** of the Hamiltonian. A ***symmetry group*** of a Hamiltonian is a group of symmetry operations of the Hamiltonian. We sometimes say that the Hamiltonian is ***invariant*** to a symmetry operation in the sense that if R is a symmetry operation the effect of R on H (not considering any function that H acts on) is to leave H unchanged.

We can easily see that the inversion E^* will also commute with the Hamiltonian operator given in Eq. (6-6). This depends on results such as those now given in Eqs. (6-20) and (6-23).

$$E^*\frac{\partial^2}{\partial X_1{}^2}\Psi_n(X_1, Y_1, Z_1, \ldots) = \frac{\partial^2}{\partial X_1{}^2}E^*\Psi_n(X_1, Y_1, Z_1, \ldots) \tag{6-20}$$

$$= \frac{\partial^2}{\partial X_1{}^2}\Psi_n(-X_1, -Y_1, -Z_1, \ldots) \tag{6-21}$$

$$= \frac{\partial^2}{\partial X_1{}^2}\Psi_n^{E^*}(X_1, Y_1, Z_1, \ldots) \tag{6-22}$$

and

$$E^* R_{rs}^{-1}\Psi_n(X_1, Y_1, Z_1, \ldots) = R_{rs}^{-1}E^*\Psi_n(X_1, Y_1, Z_1, \ldots) \qquad (6\text{-}23)$$

$$= R_{rs}^{-1}\Psi_n(-X_1, -Y_1, -Z_1, \ldots) \qquad (6\text{-}24)$$

$$= R_{rs}^{-1}\Psi_n^{E^*}(X_1, Y_1, Z_1, \ldots). \qquad (6\text{-}25)$$

Equation (6-20) follows from $\partial^2/\partial(-X_i)^2 = \partial^2/\partial X_i^2$, and Eq. (6-23) follows from the fact that R_{rs} [see Eq. (6-3)] depends only on the squares of the differences of the Cartesian coordinates and does not change if the signs of all the coordinates change (obviously the distances between the particles are unaffected by inverting the molecule).

Since any permutation of identical nuclei P commutes with H^0, and E^* commutes with H^0, it must be that $PE^* = E^*P = P^*$ commutes with H^0, i.e.,

$$P^*H^0 = PE^*H^0 = PH^0E^* = H^0PE^* = H^0P^*. \qquad (6\text{-}26)$$

Thus all the elements of the CNPI (or MS) group of a molecule will commute with the molecular Hamiltonian given in Eq. (6-6) and the CNPI (or MS) group is therefore a symmetry group of that Hamiltonian. Any element R of the CNPI (or MS) group of a molecule will convert an eigenfunction Ψ_n of H^0 into a new eigenfunction Ψ_n^R of H^0 having the same eigenvalue as Ψ_n. To proceed further we discuss the cases of nondegenerate and degenerate energy levels separately. A molecular state with energy E is said to be degenerate if more than one linearly independent eigenfunction of the molecular Hamiltonian has eigenvalue E.

6.2.1 Nondegenerate levels

If E_n is a nondegenerate eigenvalue of H^0, belonging to eigenfunction Ψ_n, then we see from Eq. (6-19) that $\Psi_2^{(12)} = (12)\Psi_n$ is also an eigenfunction of H^0 with eigenvalue E_n. For this to be true we must have

$$\Psi_n^{(12)} = c\Psi_n, \qquad (6\text{-}27)$$

where c is a constant, since Ψ_n is the *only* eigenfunction of H^0 with eigenvalue E_n (it is nondegenerate by definition). We can evaluate c as follows: Writing

$$(12)\Psi_n = c\Psi_n, \qquad (6\text{-}28)$$

and applying (12) to both sides, we obtain

$$(12)^2\Psi_n = (12)c\Psi_n. \qquad (6\text{-}29)$$

Since $(12)^2$ is the identity and (12) commutes with c (a constant) this equation can be rewritten as

$$\Psi_n = c(12)\Psi_n \qquad (6\text{-}30)$$

$$= c^2\Psi_n, \tag{6-31}$$

i.e., $c^2 = 1$, and therefore

$$c = \pm 1. \tag{6-32}$$

A nondegenerate eigenfunction of H^0 for a molecule in which 1 and 2 are identical nuclei is thus either invariant ($c = +1$) to (12) or is changed in sign ($c = -1$) by (12). Alternatively we can say that for a molecule in which 1 and 2 are identical nuclei the value of a nondegenerate eigenfunction Ψ_n at each point $(X_1, Y_1, Z_1, X_2, Y_2, Z_2, W)$ in configuration space is either equal to, or equal to the negative of, its value at each point $(X_2, Y_2, Z_2, X_1, Y_1, Z_1, W)$. Some of the nondegenerate eigenfunctions will be unaffected by (12), i.e., symmetric under (12), and all the others will be changed in sign by (12), i.e., antisymmetric under (12). We cannot determine which will be symmetric and which antisymmetric except by looking at the functions in detail.

A simple example of this is afforded by the function $\sin(X_1 - X_2)$ which is antisymmetric under (12):

$$(12)\sin(X_1 - X_2) = \sin(X_2 - X_1) = -\sin(X_1 - X_2). \tag{6-33}$$

Alternatively $\cos(X_1 - X_2)$ is symmetric under (12). The functions $\sin(X_1 - X_2)$ and $\cos(X_1 - X_2)$, and the functions used in Problems 6-1, 6-2, and 6-3 that follow, are not eigenfunctions of a molecular Hamiltonian; these functions are introduced simply as convenient functions for studying transformation properties.

To introduce some more of the definitions that are used we can take (12) together with the identity E to make the $\boldsymbol{S}_2$ group. The $\boldsymbol{S}_2$ group has two irreducible representations, which we call Γ_1 and Γ_2, and the character table of $\boldsymbol{S}_2$ is given in Table 6-1. A function that is symmetric under (12) is said to *generate* (or *form a basis for*) the representation Γ_1 of the $\boldsymbol{S}_2$ group, since application of either E or (12) to a symmetric function produces (+1) times the function, and the representation Γ_1 has (+1) as its elements both under E and (12). A function that is antisymmetric under (12) generates the numbers (+1) and (−1) under the operations E and (12), respectively, and thus generates the representation Γ_2. Symmetric functions would then be said to be of Γ_1 *symmetry* in the $\boldsymbol{S}_2$ group, while antisymmetric functions are of Γ_2 symmetry.

Table 6-1

The character table of the $\boldsymbol{S}_2$ group

$\boldsymbol{S}_2$:	E	(12)
Γ_1:	1	1
Γ_2:	1	−1

In deriving Eq. (6-32) from Eq. (6-28) for the effect of (12) on Ψ_n it was important that $(12)^2 = E$. An arbitrary operation R that commutes with the Hamiltonian need not be self-reciprocal like this and in general we have $R^m = E$ where m need not be 2. In this case we determine that for a non-degenerate eigenfunction

$$R^m \Psi_n = c^m \Psi_n = \Psi_n, \tag{6-34}$$

i.e.,

$$c = \sqrt[m]{1}. \tag{6-35}$$

For example, the operation (123) is such that $(123)^3 = E$, and nondegenerate eigenfunctions of a Hamiltonian that commutes with (123) will be multiplied by 1, $\omega = \exp(2\pi i/3)$, or ω^2 by the effect of (123).

In general any nondegenerate eigenfunction of the Hamiltonian will generate a one-dimensional representation of a symmetry group of the Hamiltonian (as is proved in Appendix 6-1 at the end of this chapter) and we say that we can *classify* the nondegenerate eigenfunction according to the one-dimensional representations of the symmetry group. We pay special attention to the effect of E^* by saying that an eigenfunction that is symmetric under it is of positive parity whereas one that is antisymmetric under it is of negative parity.

Problem 6-1. Consider the following functions for the water molecule, where 1 and 2 label the protons,

$$\Psi_1 = \sin(X_1 - X_2 + Y_1 - Y_2 + Z_1 - Z_2),$$
$$\Psi_2 = \cos(X_1 - X_2 + Y_1 - Y_2 + Z_1 - Z_2),$$

and

$$\Psi_3 = \sin(X_1 + X_2 + Y_1 + Y_2 + Z_1 + Z_2).$$

Each of these functions generates a one-dimensional representation of the CNPI group $C_{2v}(M)$ of the water molecule (see Table 6-2); determine which representations are generated.

Table 6-2

The character table of the CNPI group $C_{2v}(M)$ of the water molecule[a]

$C_{2v}(M)$:	E	(12)	E^*	$(12)^*$
A_1:	1	1	1	1
A_2:	1	1	−1	−1
B_1:	1	−1	−1	1
B_2:	1	−1	1	−1

[a] Protons labeled 1 and 2.

Answer. To determine the representation for which each Ψ_i forms a basis we must determine the coefficients c_i^R, where

$$E\Psi_i = c_i^E \Psi_i, \tag{6-36}$$

$$(12)\Psi_i = c_i^{(12)}\Psi_i, \tag{6-37}$$

$$E^*\Psi_i = c_i^{E^*}\Psi_i, \tag{6-38}$$

and

$$(12)^*\Psi_i = c_i^{(12)^*}\Psi_i. \tag{6-39}$$

The representation generated is then $[c_i^E, c_i^{(12)}, c_i^{E^*}, c_i^{(12)^*}]$. Clearly

$$c_i^E = 1, \tag{6-40}$$

since E does nothing to the functions. Also we have

$$c_i^{(12)^*} = c_i^{(12)} c_i^{E^*}, \tag{6-41}$$

since the c_i^R form a one-dimensional representation. As a result of Eqs. (6-40) and (6-41) we only have to determine $c_i^{(12)}$ and $c_i^{E^*}$ for each Ψ_i in order to determine the representation that the function generates.

We look first at Ψ_1.

$$\begin{aligned}(12)\Psi_1 &= (12)\sin(X_1 - X_2 + Y_1 - Y_2 + Z_1 - Z_2)\\ &= \sin(X_2 - X_1 + Y_2 - Y_1 + Z_2 - Z_1)\\ &= (-1)\Psi_1\end{aligned} \tag{6-42}$$

and

$$\begin{aligned}E^*\Psi_1 &= E^*\sin(X_1 - X_2 + Y_1 - Y_2 + Z_1 - Z_2)\\ &= \sin(-X_1 + X_2 - Y_1 + Y_2 - Z_1 + Z_2)\\ &= (-1)\Psi_1.\end{aligned} \tag{6-43}$$

Collecting the results for Ψ_1 we have

$$c_1^E = +1, \tag{6-44a}$$

$$c_1^{(12)} = -1, \tag{6-44b}$$

$$c_1^{E^*} = -1, \tag{6-44c}$$

and

$$c_1^{(12)^*} = c_1^{(12)} c_1^{E^*} = +1, \tag{6-44d}$$

so that the representation generated by Ψ_1 is $[+1, -1, -1, +1]$, i.e., B_1, in the CNPI group of the water molecule.

We next look at the function Ψ_2:

$$(12)\Psi_2 = \cos(X_2 - X_1 + Y_2 - Y_1 + Z_2 - Z_1) = (+1)\Psi_2 \tag{6-45}$$

and

$$E^*\Psi_2 = \cos(-X_1 + X_2 - Y_1 + Y_2 - Z_1 + Z_2) = (+1)\Psi_2, \tag{6-46}$$

and the function Ψ_2 generates the A_1 representation of the CNPI group.

Finally we look at Ψ_3.

$$(12)\Psi_3 = \sin(X_2 + X_1 + Y_2 + Y_1 + Z_2 + Z_1) = (+1)\Psi_3 \tag{6-47}$$

and

$$E^*\Psi_3 = \sin(-X_1 - X_2 - Y_1 - Y_2 - Z_1 - Z_2) = (-1)\Psi_3, \tag{6-48}$$

and the function Ψ_3 generates the representation A_2. The functions Ψ_1, Ψ_2, and Ψ_3 are thus of symmetry B_1, A_1, and A_2, respectively; Ψ_1 and Ψ_3 are of negative parity whereas Ψ_2 is of positive parity.

6.2.2 Degenerate levels

If E_n is an l-fold degenerate eigenvalue of the molecular Hamiltonian with eigenfunctions Ψ_{n1}, Ψ_{n2}, ..., Ψ_{nl}, then the effect of a symmetry operation R on one of these functions will be to convert it to a linear combination of these l functions. This must be true since the function that results by applying R to any one of these functions still has eigenvalue E_n [see Eq. (6-19) and the discussion after it], and the most general function of this type is a linear combination of these functions.

From the above remarks we see that the effect of R can be written[2] using matrix notation as

$$R\Psi_{ni} = \sum_{j=1}^{l} D[R]_{ij}\Psi_{nj}, \tag{6-49}$$

where $i = 1, 2, \ldots, l$. For example, choosing $i = 1$, we have the effect of R on Ψ_{n1} as:

$$R\Psi_{n1} = D[R]_{11}\Psi_{n1} + D[R]_{12}\Psi_{n2} + \cdots + D[R]_{1l}\Psi_{nl}. \tag{6-50}$$

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[2] **Note the order of the subscripts on $D[R]$, and see the Bibliographical Notes concerning the alternative definition used in Wigner (1959).**

The $D[R]_{ij}$ are numbers and $D[R]$ is a matrix of these numbers; the matrix $D[R]$ is *generated* by the effect of R on the l functions Ψ_{ni}. We can visualize Eq. (6-49) as a column matrix $R\Psi_n$ being equal to the product of a square matrix $D[R]$ and a column matrix Ψ_n, i.e.,

$$R\begin{bmatrix} \Psi_n \end{bmatrix} = \begin{bmatrix} & D[R] & \end{bmatrix}\begin{bmatrix} \Psi_n \end{bmatrix}. \tag{6-51}$$

Each operation in a symmetry group of the Hamiltonian will generate such an $l \times l$ matrix, and it is shown in Appendix 6-1 that if three operations of the group P_1, P_2, and P_{12} are related by

$$P_1 P_2 = P_{12} \tag{6-52}$$

then the matrices generated by application of them to the Ψ_{ni} [as described by Eq. (6-49)] will satisfy

$$D[P_1]D[P_2] = D[P_{12}]. \tag{6-53}$$

Thus the matrices will have a multiplication table with the same structure as the multiplication table of the symmetry group and hence will form an l-dimensional representation of the group.

A given l-fold degenerate state may generate a reducible or an irreducible l-dimensional representation of the symmetry group considered. If the representation is irreducible then the degeneracy is said to be ***necessary***, i.e., imposed by the symmetry of the Hamiltonian. However, if the representation is reducible then the degeneracy between the different states is said to be accidental, and it is not imposed by the symmetry of the Hamiltonian.[3]

Suppose that, for the given l-fold degenerate energy level E_n, we choose a different set of l linearly independent functions, i.e., use Φ_{nk} instead of Ψ_{ni}, where

$$\Phi_{nk} = \sum_{i=1}^{l} A_{ki}\Psi_{ni} \tag{6-54}$$

and A is an orthogonal matrix. Such a transformation is called an orthogonal transformation, and if the Ψ_{ni} are eigenfunctions of the Hamiltonian with eigenvalue E_n then the Φ_{nk} will also be eigenfunctions having the same eigenvalue. The eigenfunctions for a given degenerate energy level are therefore arbitrary to the extent of an orthogonal transformation. The question arises: Which representation of the symmetry group of the Hamiltonian will the new functions Φ_{nk} generate? The matrix representing the operation R that is generated by the new functions Φ_{nk} will be given by

$$R\Phi_{nk} = \sum_{r=1}^{l} \bar{D}[R]_{kr}\Phi_{nr}. \tag{6-55}$$

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[3] **But it might indicate that a symmetry operation for the Hamiltonian has been forgotten.**

Applying R to both sides of Eq. (6-54) we obtain

$$R\Phi_{nk} = \sum_{i=1}^{l} A_{ki} R\Psi_{ni}. \tag{6-56}$$

Using Eq. (6-49) we can write Eq. (6-56) as

$$R\Phi_{nk} = \sum_{i=1}^{l} A_{ki} \sum_{j=1}^{l} D[R]_{ij} \Psi_{nj}. \tag{6-57}$$

The inverse of Eq. (6-54) can be written as

$$\Psi_{nj} = \sum_{r=1}^{l} (A^{-1})_{jr} \Phi_{nr} \tag{6-58}$$

and substituting this equation into Eq. (6-57) we obtain

$$R\Phi_{nk} = \sum_{i=1}^{l} A_{ki} \sum_{j=1}^{l} D[R]_{ij} \sum_{r=1}^{l} (A^{-1})_{jr} \Phi_{nr} \tag{6-59}$$

$$= \sum_{i,j,r} A_{ki} D[R]_{ij} (A^{-1})_{jr} \Phi_{nr}. \tag{6-60}$$

From Eqs. (6-60) and (6-55) we obtain the matrix equation

$$\bar{D}[R] = AD[R]A^{-1}. \tag{6-61}$$

Thus the matrix representation generated by the Φ_n, containing $\bar{D}$, is obtained from that generated by the Ψ_n by performing the similarity transformation of Eq. (6-61) with the matrix A, and these representations are, therefore, equivalent. This means that the representation generated by the eigenfunctions of a particular degenerate energy level is unique (apart from a similarity transformation) and can be unambiguously reduced to its irreducible components. Therefore, each energy level can be labeled according to the irreducible representations of the symmetry group, and this is an important characteristic of use in distinguishing the energy levels.

Using l mutually orthogonal functions[4] to describe an l-fold degenerate level it can be shown that the matrix representation obtained will be unitary, i.e.,

$$D[R^{-1}]_{ij} = D[R]^{*}_{ji}. \tag{6-62}$$

We always use orthonormal wavefunctions and hence always obtain unitary representations of the symmetry group.

---

[4] Two functions Ψ_{ni} and Ψ_{nj} are orthogonal if the product $\Psi_{ni}{}^{*}\Psi_{nj}$, integrated over all configuration space, vanishes. A function Ψ is normalized if the product $\Psi^{*}\Psi$ integrated over all configuration space is unity. An orthonormal set contains functions that are normalized and orthogonal to each other.

6.3 PROJECTION OPERATORS

We frequently consider a set of functions, $\Phi_1, \ldots, \Phi_r$, say, which generates a reducible representation Γ of a symmetry group, i.e., for a particular operation R of the group we have

$$R\Phi_n = \sum_{m=1}^{r} D^{\Gamma}[R]_{nm}\Phi_m, \tag{6-63}$$

where the $D^{\Gamma}[R]$ are the matrices of the reducible representation Γ. We wish to determine which linear combinations of the functions Φ_n transform according to the irreducible representations Γ_i that make up Γ. To do this we use a *projection operator*.[5] Each irreducible representation of the group has different projection operators, and we need to know the elements of the irreducible representation matrices $D^{\Gamma_i}[R]$ in order to be able to construct the projection operators. Written in their most general form, the projection operators used here are particular combinations of the operations in the group defined by the equation

$$P^{\Gamma_i}_{mm} = \frac{l_i}{h}\sum_R D^{\Gamma_i}[R]^*_{mm}R, \tag{6-64}$$

where l_i is the dimension of Γ_i, h is the order of the group, $D^{\Gamma_i}[R]_{mm}$ is a diagonal element of the matrix $D^{\Gamma_i}[R]$ in the irreducible representation Γ_i as used in the orthogonality relation Eq. (5-40), and the sum is over all operations in the group. As shown in Appendix 6-2 the required functions Ψ_{im} are obtained by applying the projection operator $P^{\Gamma_i}_{mm}$ to a function Φ_n which transforms according to the reducible representation Γ:

$$\begin{aligned} P^{\Gamma_i}_{mm}\Phi_n &= \frac{l_i}{h}\sum_R D^{\Gamma_i}[R]^*_{mm}R\Phi_n \\ &= \frac{l_i}{h}\sum_{R,k} D^{\Gamma_i}[R]^*_{mm}D^{\Gamma}[R]_{nk}\Phi_k \\ &= \Psi_{im}. \end{aligned} \tag{6-65}$$

The functions Ψ_{im}, $m = 1, 2, 3, \ldots, l_i$, transform according to

$$R\Psi_{im} = \sum_{s=1}^{l_i} D^{\Gamma_i}[R]_{ms}\Psi_{is}, \tag{6-66}$$

and generate the matrices $D^{\Gamma_i}[R]$ [see Eq. (6-49)]. The function Ψ_{im} transforms irreducibly as the m'th row of Γ_i. Some examples of the application of projection operators are given in Problems 6-2 and 6-3. If in the reduction of the representation Γ generated by the functions Φ_n the irreducible representation Γ_i does not occur then the effect of P^{Γ_i} on Φ_n will be to give zero; i.e., the projection operator *annihilates* Φ_n. The reader can test this by applying the operator P^{A_1} to any of the three functions Ψ_a, Ψ_b, or Ψ_c in Problem 6-2 which follows.

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[5] The general definition of a projection operator requires it to be Hermitian [see Eq. (6-152)] and *idempotent*. An idempotent operator $\hat{P}$ is such that $\hat{P}^2 = \hat{P}$. The particular projection operators discussed here fulfill these conditions.

For a one-dimensional irreducible representation Γ_i, the representation matrices $D^{\Gamma_i}[R]$ have only one element $D^{\Gamma_i}[R]_{11} = \chi^{\Gamma_i}[R]$, the character for the operation R. In this case, we can write the projection operator as

$$P^{\Gamma_i} = \frac{1}{h}\sum_R \chi^{\Gamma_i}[R]^* R. \tag{6-67}$$

For an l_i-fold degenerate irreducible representation we can define

$$P^{\Gamma_i} = \sum_{m=1}^{l_i} P^{\Gamma_i}_{mm} = \frac{l_i}{h}\sum_R \chi^{\Gamma_i}[R]^* R. \tag{6-68}$$

When applied to the function Φ_n, the projection operator P^{Γ_i} for a degenerate irreducible representation will produce a function belonging to Γ_i, but the transformation properties of this function under the operations R will not be known. However, to construct this projection operator we only need the characters of the irreducible representations.

An operator related to the projection operator $P^{\Gamma_i}_{mm}$ is the so-called *transfer operator*

$$P^{\Gamma_i}_{mt} = \frac{l_i}{h}\sum_R D^{\Gamma_i}[R]^*_{mt} R, \tag{6-69}$$

where $t \neq m$ so that this operator involves the off-diagonal elements of the matrices $D^{\Gamma_i}[R]$. We show in Appendix 6-2 that if we have already determined a function Ψ_{im} which belongs to the m'th row of Γ_i, then by applying $P^{\Gamma_i}_{mt}$ to this function

$$P^{\Gamma_i}_{mt}\Psi_{im} = \Psi_{it}, \tag{6-70}$$

we can generate a function Ψ_{it} which belongs to the t'th row of Γ_i.

Problem 6-2. The character table of the MS group $C_{3v}(M)$ of the CH_3F molecule is given in Table 6-3. We label the irreducible representations A_1, A_2, and E. Suppose that Ψ_a, Ψ_b, and Ψ_c are threefold degenerate orthonormal eigenfunctions for CH_3F where

$$\Psi_a = X_1, \quad \Psi_b = X_2, \quad \text{and} \quad \Psi_c = X_3,$$

where the protons are labeled 1, 2, and 3. Which representation of the $C_{3v}(M)$ group do these three functions generate? Reduce the representation obtained to its irreducible components, and find the combinations of the functions that generate these irreducible representations by using the projection operator technique. Equations (1-11)-(1-13) and (2-9)-(2-10) will be of use in solving this problem. In this artificial example we are, for the sake of clarity, taking the functions X_i (the nuclear coordinates) as being normalized and orthogonal to each other; it would be more correct to take three identical (normalized and orthogonal) *functions* of X_1, X_2, and X_3 instead of X_1, X_2, and X_3, respectively.

Table 6-3

The character table of the MS group $C_{3v}(M)$ of the methyl fluoride molecule[a]

$C_{3v}(M)$:	E	(123) (132)	(12)* (23)* (13)*
A_1:	1	1	1
A_2:	1	1	−1
E:	2	−1	0

[a] The protons are labeled 1 2, and 3.

Answer. We must determine the 3 × 3 matrices $D[R]$ generated by the effect of the operations R of the $C_{3v}(M)$ group on the three functions (Ψ_a, Ψ_b, Ψ_c). We consider (123) and (12)* in detail with the help of Eqs. (1-12) and (2-9).

$$(123)\Psi_a = (123)X_1 = X_3 = \Psi_c, \tag{6-71}$$

$$(123)\Psi_b = (123)X_2 = X_1 = \Psi_a, \tag{6-72}$$

and

$$(123)\Psi_c = \Psi_b, \tag{6-73}$$

so that

$$(123)\begin{bmatrix}\Psi_a\\ \Psi_b\\ \Psi_c\end{bmatrix} = \begin{bmatrix}\Psi_c\\ \Psi_a\\ \Psi_b\end{bmatrix} = \underbrace{\begin{bmatrix}0 & 0 & 1\\ 1 & 0 & 0\\ 0 & 1 & 0\end{bmatrix}}_{D[(123)]}\begin{bmatrix}\Psi_a\\ \Psi_b\\ \Psi_c\end{bmatrix}. \tag{6-74}$$

Also,

$$(12)^*\Psi_a = (12)^*X_1 = -X_2 = -\Psi_b, \tag{6-75}$$

$$(12)^*\Psi_b = -\Psi_a, \tag{6-76}$$

and

$$(12)^*\Psi_c = -\Psi_c, \tag{6-77}$$

so that

$$(12)^* \begin{bmatrix} \Psi_a \\ \Psi_b \\ \Psi_c \end{bmatrix} = \begin{bmatrix} -\Psi_b \\ -\Psi_a \\ -\Psi_c \end{bmatrix} = \underbrace{\begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}}_{D[(12)^*]} \begin{bmatrix} \Psi_a \\ \Psi_b \\ \Psi_c \end{bmatrix}. \tag{6-78}$$

Similarly the operations (132), $(23)^*$, and $(13)^*$ generate the matrices

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}, \quad \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{bmatrix}, \quad \text{and} \quad \begin{bmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{bmatrix}, \tag{6-79}$$

respectively, and E generates the 3×3 unit matrix. These matrices form a representation of the $C_{3v}(M)$ group as the reader can test by forming their multiplication table. The characters of this representation are

$$\begin{aligned} &\chi[E] = 3, \qquad \chi[(123)] = \chi[(132)] = 0, \\ &\chi[(12)^*] = \chi[(23)^*] = \chi[(13)^*] = -1. \end{aligned} \tag{6-80}$$

By inspection of Table 6-3, or by using Eq. (5-45), we see that this representation reduces to $A_2 \oplus E$.

The combinations of the functions Ψ_a, Ψ_b, and Ψ_c that are of species A_2 and E are found by using projection operators. An unnormalized combination of species A_2 is given by

$$\Phi'(A_2) = \left\{ \frac{1}{6} \sum_R \chi^{A_2}[R]^* R \right\} \Psi_a, \tag{6-81}$$

where the operator in the braces is the A_2 projection operator P^{A_2} from Eq. (6-67). Operating with P^{A_2} on Ψ_a we have

$$\begin{aligned} \Phi'(A_2) &= \frac{1}{6}\Big\{(+1) \times E\Psi_a + (+1) \times (123)\Psi_a + (+1) \times (132)\Psi_a \\ &\quad + (-1) \times (12)^*\Psi_a + (-1) \times (23)^*\Psi_a + (-1) \times (13)^*\Psi_a\Big\} \\ &= \frac{1}{6}\Big\{(+1)\Psi_a + (+1)\Psi_c + (+1)\Psi_b + (-1)(-\Psi_b) \\ &\quad + (-1)(-\Psi_a) + (-1)(-\Psi_c)\Big\} \\ &= \frac{1}{3}(\Psi_a + \Psi_b + \Psi_c). \end{aligned} \tag{6-82}$$

Normalizing we obtain

$$\Phi(A_2) = (\Psi_a + \Psi_b + \Psi_c)/\sqrt{3} = (X_1 + X_2 + X_3)/\sqrt{3}. \tag{6-83}$$

The same function would be obtained if we applied P^{A_2} to Ψ_b or Ψ_c. The reader should notice that P^{A_1} annihilates Ψ_a, Ψ_b, or Ψ_c since the representation generated by these functions does not contain A_1.

In order that we can use the projection operators P_{11}^E and P_{22}^E [Eq. (6-64)] and the transfer operators P_{12}^E and P_{21}^E [Eq. (6-69)], we must determine a group of representation matrices $D^E[R]$ for the irreducible representation E. It so happens that we already know such a matrix group from Chapter 5. The MS group $\boldsymbol{C}_{3v}(\mathrm{M})$ is isomorphic to the permutation group $\boldsymbol{S}_3$ defined in Chapter 1 [see Table 1-1], and the correspondence between the elements is as follows

$$\begin{array}{lcccccc} \boldsymbol{S}_3: & E & (123) & (132) & (12) & (23) & (13) \\ \boldsymbol{C}_{3v}(\mathrm{M}): & E & (123) & (132) & (12)^* & (23)^* & (13)^*. \end{array} \tag{6-84}$$

The reader should prove this by showing that the multiplication table of $\boldsymbol{C}_{3v}(\mathrm{M})$ can be obtained from that of $\boldsymbol{S}_3$ [Table 1-1] by simply replacing (12), (23), and (13) by $(12)^*$, $(23)^*$, and $(13)^*$, respectively. In Eq. (5-27) we have given a group Γ_3 of 2 × 2 matrices; this group is isomorphic to $\boldsymbol{S}_3$ so that it is also isomorphic to $\boldsymbol{C}_{3v}(\mathrm{M})$ with the following mapping:

$$\begin{array}{lccc} \boldsymbol{C}_{3v}(\mathrm{M}): & E & (123) & (132) \\ \Gamma_3: & \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} & \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}. \\ \\ \boldsymbol{C}_{3v}(\mathrm{M}): & (12)^* & (23)^* & (13)^* \\ \Gamma_3: & \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} & \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} & \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} \end{array} \tag{6-85}$$

The reader can also check that the traces of these matrices are equal to the characters of the E irreducible representation in Table 6-3; the matrices obviously form the desired group of representation matrices $D^E[R]$. From Eq. (6-64) we have

$$P_{11}^E = \frac{1}{3}\sum_R D^E[R]_{11}^* R, \tag{6-86}$$

and operating with this operator on Ψ_a yields

$$\begin{aligned}\Phi_1'(E) &= \frac{1}{3}\Big\{(+1)\times E\Psi_a + (-1/2)\times(123)\Psi_a + (-1/2)\times(132)\Psi_a \\ &\quad + (+1)\times(12)^*\Psi_a + (-1/2)\times(23)^*\Psi_a + (-1/2)\times(13)^*\Psi_a\Big\} \\ &= \frac{1}{3}\Big\{(+1)\Psi_a + (-1/2)\Psi_c + (-1/2)\Psi_b + (+1)(-\Psi_b) \\ &\quad + (-1/2)(-\Psi_a) + (-1/2)(-\Psi_c)\Big\} = \frac{1}{2}(\Psi_a - \Psi_b),\end{aligned} \tag{6-87}$$

which on normalizing gives

$$\Phi_1(E) = (X_1 - X_2)/\sqrt{2}. \tag{6-88}$$

From Eq. (6-70) we see that we can obtain the partner function of $\Phi_1(E)$, $\Phi_2(E)$, by applying the transfer operator P_{12}^E [Eq. (6-69)] to $\Phi_1(E)$:

$$\begin{aligned}P_{12}^E\Phi_1(E) &= \frac{1}{3}\Big\{(0)\times E\Phi_1(E) + (\sqrt{3}/2)\times(123)\Phi_1(E) \\ &\quad + (-\sqrt{3}/2)\times(132)\Phi_1(E) + (0)\times(12)^*\Phi_1(E) \\ &\quad + (\sqrt{3}/2)\times(23)^*\Phi_1(E) + (-\sqrt{3}/2)\times(13)^*\Phi_1(E)\Big\} \\ &= \frac{1}{3}\Big\{(\sqrt{3}/2)(1/\sqrt{2})(\Psi_c - \Psi_a) + (-\sqrt{3}/2)(1/\sqrt{2})(\Psi_b - \Psi_c) \\ &\quad + (\sqrt{3}/2)(1/\sqrt{2})(-\Psi_a + \Psi_c) + (-\sqrt{3}/2)(1/\sqrt{2})(-\Psi_c + \Psi_b)\Big\} \\ &= (1/\sqrt{6})(2\Psi_c - \Psi_a - \Psi_b).\end{aligned} \tag{6-89}$$

This function is normalized. We thus have

$$\Phi_2(E) = \frac{1}{\sqrt{6}}(2X_3 - X_1 - X_2). \tag{6-90}$$

The two functions $\Phi_1(E)$ and $\Phi_2(E)$ belong to the first and second rows, respectively, of the irreducible representation E of the $C_{3v}(\mathrm{M})$ group. We can also obtain a function belonging to the second row of E by letting P_{22}^E operate on Ψ_a, and the result is

$$P_{22}^E\Psi_a = -(2X_3 - X_1 - X_2)/6 = -\frac{1}{\sqrt{6}}\Phi_2(E). \tag{6-91}$$

This function differs from $\Phi_2(E)$ by a factor of $-1/\sqrt{6}$. This factor is an expansion coefficient in the expansion of Ψ_a in terms of the symmetrized functions $[\Phi(A_2), \Phi_1(E), \Phi_2(E)]$ [i.e., the expansion coefficient $A_{n,im}$ in Eq. (6-181)].

The reader can test that the three functions $\Phi(A_2)$ and $[\Phi_1(E), \Phi_2(E)]$, transform separately as A_2 and E by applying the operations of the $C_{3v}(\mathrm{M})$ group to them (see Appendix 6-3).

6.3.1 Projection operators for a direct product group

The projection operator formalism discussed in Section 6.3 takes on a particularly simple form for direct product groups [see Sections 5.7 and 5.8.2]. For an irreducible representation $\Gamma_{ij}^{(G)}$ [see Section 5.8.2] of a group $\boldsymbol{G}$, which is the direct product of two invariant subgroups $\boldsymbol{A}$ and $\boldsymbol{B}$ as given by Eq. (5-70), the projection operator in Eq. (6-68) has the form

$$\begin{aligned} P^{\Gamma_{ij}^{(G)}} &= \frac{l_i^{(A)} l_j^{(B)}}{ab} \sum_R \chi^{\Gamma_{ij}^{(G)}} [R]^* R \\ &= \frac{l_i^{(A)} l_j^{(B)}}{ab} \sum_{R^{(A)}, R^{(B)}} \chi^{\Gamma_i^{(A)}} \left[R^{(A)}\right]^* \chi^{\Gamma_j^{(B)}} \left[R^{(B)}\right]^* R^{(A)} R^{(B)} \\ &= \left(\frac{l_i^{(A)}}{a} \sum_{R^{(A)}} \chi^{\Gamma_i^{(A)}} \left[R^{(A)}\right]^* R^{(A)} \right) \left(\frac{l_j^{(B)}}{b} \sum_{R^{(B)}} \chi^{\Gamma_j^{(B)}} \left[R^{(B)}\right]^* R^{(B)} \right). \end{aligned} \tag{6-92}$$

In Eq. (6-92), a is the order of $\boldsymbol{A}$ and b is the order of $\boldsymbol{B}$. Each element of $\boldsymbol{G}$ is written as $R = R^{(A)} R^{(B)}$, where $R^{(A)}$ is an element of $\boldsymbol{A}$ and $R^{(B)}$ an element of $\boldsymbol{B}$. The irreducible representation $\Gamma_{ij}^{(G)} = (\Gamma_i^{(A)}, \Gamma_j^{(B)})$ [Eq. (5-71)], where $\Gamma_i^{(A)}$ (with dimension $l_i^{(A)}$) and $\Gamma_j^{(B)}$ (with dimension $l_j^{(B)}$) are irreducible representations of $\boldsymbol{A}$ and $\boldsymbol{B}$, respectively, with characters $\chi^{\Gamma_i^{(A)}}[R^{(A)}]$ and $\chi^{\Gamma_j^{(B)}}[R^{(B)}]$.

In the derivation of Eq. (6-92) we have made use of the facts that $\boldsymbol{G}$ has the order ab and that the irreducible representation $\Gamma_{ij}^{(G)}$ is $l_i^{(A)} l_j^{(B)}$-fold degenerate. We have also inserted the expression in Eq. (5-72) for the characters associated with $\Gamma_{ij}^{(G)}$. Comparison of the last line in Eq. (6-92) with Eq. (6-68) shows that the projection operator $P^{\Gamma_{ij}^{(G)}}$ is the product of two projection operators, one for the irreducible representation $\Gamma_i^{(A)}$ of $\boldsymbol{A}$ and one for the irreducible representation $\Gamma_j^{(B)}$ of $\boldsymbol{B}$. The two projection operators commute because all elements in $\boldsymbol{A}$ commute with all elements in $\boldsymbol{B}$ [see Sections 5.7 and 5.8.2]. The form of $P^{\Gamma_{ij}^{(G)}}$ implies that in order for a wavefunction to transform irreducibly in $\boldsymbol{G}$ according to $\Gamma_{ij}^{(G)}$ it must transform irreducibly in $\boldsymbol{A}$ and $\boldsymbol{B}$ simultaneously according to the irreducible representations $\Gamma_i^{(A)}$ and $\Gamma_j^{(B)}$, respectively. A derivation slightly more involved than that given here shows that the projection operators $P^{\Gamma_i}_{mm}$ [which involve elements of the representation matrices rather than the characters; see Eq. (6-64)] for a direct product group also factorize in the manner given in Eq. (6-92). That is, we can 'symmetrize' wavefunctions in $\boldsymbol{G}$ by 'symmetrizing' them separately in $\boldsymbol{A}$ and $\boldsymbol{B}$ when $\boldsymbol{G}$ is the direct product of $\boldsymbol{A}$ and $\boldsymbol{B}$. We use this result several times in the book [see, for example, Table 16-11].

6.4 THE SYMMETRY OF A PRODUCT

Given an s-fold degenerate state of energy E_n and symmetry Γ_n, with eigenfunctions $\Phi_{n1}, \Phi_{n2}, \ldots, \Phi_{ns}$, and an r-fold degenerate state of energy E_m and symmetry Γ_m, with eigenfunctions $\Phi_{m1}, \Phi_{m2}, \ldots, \Phi_{mr}$, we wish to determine the symmetry Γ_{mn} of the set of functions $\Psi_{ij} = \Phi_{ni}\Phi_{mj}$, where $i = 1, 2, \ldots, s$ and $j = 1, 2, \ldots, r$. There will be $s \times r$ functions of the type Ψ_{ij}. The matrices D^{Γ_n} and D^{Γ_m} in the representations Γ_n and Γ_m, respectively, are obtained from

$$R\Phi_{ni} = \sum_{k=1}^{s} D^{\Gamma_n}[R]_{ik}\Phi_{nk} \tag{6-93}$$

and

$$R\Phi_{mj} = \sum_{l=1}^{r} D^{\Gamma_m}[R]_{jl}\Phi_{ml}, \tag{6-94}$$

where R is an operation of the symmetry group. To obtain the matrices in the representation Γ_{nm} we write

$$R[\Phi_{ni}\Phi_{mj}] = \sum_{k=1}^{s}\sum_{l=1}^{r} D^{\Gamma_n}[R]_{ik}D^{\Gamma_m}[R]_{jl}\Phi_{nk}\Phi_{ml} \tag{6-95}$$

and we can write this as

$$R\Psi_{ij} = \sum_{k,l=1,1}^{s,r} D^{\Gamma_{nm}}[R]_{ij,kl}\Psi_{kl}. \tag{6-96}$$

From this we see that the $s \times r$ dimensional representation Γ_{nm} generated by the $s \times r$ functions Ψ_{ij} has matrices with elements given by

$$D^{\Gamma_{nm}}[R]_{ij,kl} = D^{\Gamma_n}[R]_{ik}D^{\Gamma_m}[R]_{jl}, \tag{6-97}$$

where each element of $D^{\Gamma_{nm}}$ is indexed by a row label ij and a column label kl, each of which runs over $s \times r$ values. The ij, ij diagonal element is given by

$$D^{\Gamma_{nm}}[R]_{ij,ij} = D^{\Gamma_n}[R]_{ii}D^{\Gamma_m}[R]_{jj}, \tag{6-98}$$

and the character of the matrix is given by

$$\chi^{\Gamma_{nm}}[R] = \sum_{i,j=1,1}^{s,r} D^{\Gamma_{nm}}[R]_{ij,ij} = \sum_{i,j=1,1}^{s,r} D^{\Gamma_n}[R]_{ii} D^{\Gamma_m}[R]_{jj}$$

$$= \chi^{\Gamma_n}[R]\chi^{\Gamma_m}[R]. \tag{6-99}$$

We can therefore calculate the character, under a symmetry operation R, in the representation generated by the product of two sets of functions, by multiplying together the characters under R in the representations generated by each of the sets of functions. We write Γ_{nm} symbolically as

$$\Gamma_{nm} = \Gamma_n \otimes \Gamma_m, \tag{6-100}$$

where the characters satisfy Eq. (6-99) in which usual algebraic multiplication is used. Knowing the character in Γ_{nm} from Eq. (6-99) we can then reduce the representation to its irreducible components using Eq. (5-45). Suppose Γ_{nm} can be reduced to irreducible representations Γ_1, Γ_2, and Γ_3 according to

$$\Gamma_n \otimes \Gamma_m = 3\Gamma_1 \oplus \Gamma_2 \oplus 2\Gamma_3. \tag{6-101}$$

In this circumstance we say that Γ_{nm} *contains* Γ_1, Γ_2, and Γ_3; since $\Gamma_n \otimes \Gamma_m$ contains Γ_1, for example, we write

$$\Gamma_n \otimes \Gamma_m \supset \Gamma_1. \tag{6-102}$$

Problem 6-3. Determine the representation generated by the product $\Phi(A_2) \times [\Phi_1(E), \Phi_2(E)]$ where these functions are given in Eqs. (6-83), (6-88), and (6-90). If we introduce

$$\theta_a(E) = (Y_1 - Y_2)/\sqrt{2} \text{ and } \theta_b(E) = (2Y_3 - Y_1 - Y_2)/\sqrt{6}$$

what is the symmetry of the product

$$[\Phi_1(E), \Phi_2(E)] \times [\theta_a(E), \theta_b(E)]?$$

Also determine the symmetry of the product

$$[\Phi_1(E), \Phi_2(E)] \times [\Phi_1(E), \Phi_2(E)].$$

Answer. The functions formed by multiplying $\Phi(A_2)$ and $[\Phi_1(E), \Phi_2(E)]$ are $\Phi(A_2)\ \Phi_1(E)$ and $\Phi(A_2)\ \Phi_2(E)$. These will transform according to a representation $\Gamma^{(1)}$, say, where by using Eq. (6-99) we deduce that the characters in $\Gamma^{(1)}$ are as follows:

$$\chi^{\Gamma^{(1)}}[E] = \chi^{A_2}[E] \times \chi^{E}[E] = 1 \times 2 = 2, \tag{6-103}$$

$$\chi^{\Gamma^{(1)}}[(123)] = \chi^{A_2}[(123)] \times \chi^{E}[(123)] = 1 \times (-1) = -1, \tag{6-104}$$

and

$$\chi^{\Gamma^{(1)}}[(12)^*] = \chi^{A_2}[(12)^*] \times \chi^{E}[(12)^*] = (-1) \times 0 = 0. \qquad (6\text{-}105)$$

We have chosen one element from each class in the $\boldsymbol{C}_{3\mathrm{v}}(\mathrm{M})$ group and we see that the representation generated is the irreducible representation E. We write

$$A_2 \otimes E = E. \qquad (6\text{-}106)$$

We deduce that $[\Phi(A_2)\Phi_1(E), \Phi(A_2)\Phi_2(E)]$ transforms according to the E representation of the $\boldsymbol{C}_{3\mathrm{v}}(\mathrm{M})$ group.

When we multiply $[\Phi_1(E), \Phi_2(E)]$ and $[\theta_a(E), \theta_b(E)]$ together we obtain the four functions $[\Phi_1\theta_a, \Phi_1\theta_b, \Phi_2\theta_a, \Phi_2\theta_b]$ and these functions will form the basis for the representation $\Gamma^{(2)}$, say, where [using Eq. (6-99)] the characters in this representation are given by

$$\chi^{\Gamma^{(2)}}[E] = \chi^{E}[E] \times \chi^{E}[E] = 4, \qquad (6\text{-}107)$$

$$\chi^{\Gamma^{(2)}}[(123)] = \chi^{E}[(123)] \times \chi^{E}[(123)] = 1, \qquad (6\text{-}108)$$

and

$$\chi^{\Gamma^{(2)}}[(12)^*] = \chi^{E}[(12)^*] \times \chi^{E}[(12)]^* = 0. \qquad (6\text{-}109)$$

Thus $\Gamma^{(2)}$ has characters [4, 1, 0]. This reduces to $A_1 \oplus A_2 \oplus E$ and we write

$$E \otimes E = A_1 \oplus A_2 \oplus E. \qquad (6\text{-}110)$$

It is left as an exercise for the reader to show, by using projection operators, that the combinations of the product functions that transform irreducibly are

$$(\Phi_1\theta_a + \Phi_2\theta_b) : A_1, \qquad (6\text{-}111)$$

$$(\Phi_1\theta_b - \Phi_2\theta_a) : A_2, \qquad (6\text{-}112)$$

and

$$[(\Phi_1\theta_a - \Phi_2\theta_b), (\Phi_1\theta_b + \Phi_2\theta_a)] : E. \qquad (6\text{-}113)$$

The three ***symmetric product functions*** $\Phi_1\theta_a, \Phi_2\theta_b$ and $(\Phi_1\theta_b + \Phi_2\theta_a)$ generate the representation $A_1 \oplus E$, and the ***antisymmetric product function***, defined as $(\Phi_1\theta_b - \Phi_2\theta_a)$, generates the representation A_2.

We now consider the product $[\Phi_1(E), \Phi_2(E)] \times [\Phi_1(E), \Phi_2(E)]$. This product gives us the functions $[\Phi_1\Phi_1, \Phi_1\Phi_2, \Phi_2\Phi_1, \Phi_2\Phi_2]$ and we might expect, from Eq. (6-110), that these four functions would transform as $A_1 \oplus A_2 \oplus E$. However, $\Phi_1\Phi_2 = \Phi_2\Phi_1$, and there are only three independent functions in the product. From Eq. (6-112) we see that the antisymmetric product function vanishes, and the three independent functions in the product (of necessity symmetric product functions) transform as $A_1 \oplus E$.

We can extend the product by introducing the functions

$$\Psi_a(E) = (Z_1 - Z_2)/\sqrt{2}, \tag{6-114}$$

and

$$\Psi_b(E) = (2Z_3 - Z_1 - Z_2)/\sqrt{6}, \tag{6-115}$$

and we can form the product $[\Phi_1, \Phi_2] \times [\theta_a, \theta_b] \times [\Psi_a, \Psi_b]$. These eight functions generate the representation

$$E \otimes E \otimes E = E \otimes (A_1 \oplus A_2 \oplus E) = A_1 \oplus A_2 \oplus 3E. \tag{6-116}$$

On the other hand if we form the product $[\Phi_1, \Phi_2] \times [\Phi_1, \Phi_2] \times [\Phi_1, \Phi_2]$ we obtain the four independent functions $\Phi_1\Phi_1\Phi_1$, $\Phi_1\Phi_1\Phi_2$, $\Phi_1\Phi_2\Phi_2$, and $\Phi_2\Phi_2\Phi_2$; these four functions transform as $A_1 \oplus A_2 \oplus E$.

The solution to Problem 6-3 provides examples of the ***symmetric product representation*** and the ***antisymmetric product representation*** of a representation with itself. The symmetric product of a doubly degenerate representation, E, say, of any group is the representation generated by the functions $\Phi_1\theta_a$, $\Phi_2\theta_b$ and $(\Phi_1\theta_b + \Phi_2\theta_a)$, where (Φ_1, Φ_2) and (θ_a, θ_b) are each of species E; the antisymmetric product is generated by $(\Phi_1\theta_b - \Phi_2\theta_a)$. In the group $\boldsymbol{C}_{3\mathrm{v}}(\mathrm{M})$ the product representation $E \otimes E$ is reducible into the sum of $A_1 \oplus E$ and A_2, where the former is the symmetric product and the latter is the antisymmetric product. We write the symmetric product as

$$[E]^2 = [E \otimes E] = A_1 \oplus E \tag{6-117}$$

and the antisymmetric product as

$$\{E\}^2 = \{E \otimes E\} = A_2. \tag{6-118}$$

In general the product of any doubly degenerate representation E with itself is reducible to the sum of the symmetric product representation $[E \otimes E]$ and the antisymmetric product representation $\{E \otimes E\}$ where the characters in the symmetric product are given by

$$\chi^{[E\otimes E]}[R] = \frac{1}{2}((\chi^E[R])^2 + \chi^E[R^2]), \tag{6-119}$$

and the characters in the antisymmetric product are given by

$$\chi^{\{E\otimes E\}}[R] = \frac{1}{2}((\chi^E[R])^2 - \chi^E[R^2]). \tag{6-120}$$

The characters in the symmetric nth power of E (i.e., the symmetry of the set of $n + 1$ independent functions obtained by taking the nth power of a pair of

E functions) can be obtained from the characters in the symmetric $(n-1)$th power of E by using (where E is doubly degenerate)

$$\chi^{[E]^n}[R] = \frac{1}{2}(\chi^E[R]\chi^{[E]^{n-1}}[R] + \chi^E[R^n]). \tag{6-121}$$

An example with $n = 3$ is given at the end of the solution to Problem 6-3. In Eqs. (6-119)-(6-121), $\chi^E[R^n]$ is the number obtained by determining the character in E under the operation $P = R^n$. The symmetric nth power of a representation is used in determining the species of vibrational wavefunctions in Chapter 12 [see Eqs. (12-58) and (12-60)].

In considering the symmetry of a product there is one especially important result, namely that the product representation Γ of two irreducible representations[6] Γ_n^* and Γ_m contains the totally symmetric representation $\Gamma^{(s)}$ once if $\Gamma_n = \Gamma_m$, otherwise the product does not contain $\Gamma^{(s)}$. This can be proved as follows. The character under the operation R in the representation Γ is given by

$$\chi^{\Gamma}[R] = \chi^{\Gamma_n}[R]^*\chi^{\Gamma_m}[R] \tag{6-122}$$

from Eq. (6-99). The number of times the totally symmetric representation occurs is given by

$$a^{\Gamma^{(s)}} = \frac{1}{h}\sum_R \chi^{\Gamma}[R] \tag{6-123}$$

from Eq. (5-45) since $\chi^{\Gamma^{(s)}}[R] = 1$ for all R. Substituting Eq. (6-122) into Eq. (6-123) we obtain

$$a^{\Gamma^{(s)}} = \frac{1}{h}\sum_R \chi^{\Gamma_n}[R]^*\chi^{\Gamma_m}[R]. \tag{6-124}$$

Using Eq. (5-41) we derive

$$a^{\Gamma^{(s)}} = \delta_{nm}, \tag{6-125}$$

i.e.,

$$a^{\Gamma^{(s)}} = 1 \qquad \text{if } \Gamma_n = \Gamma_m$$

or

$$a^{\Gamma^{(s)}} = 0 \qquad \text{if } \Gamma_n \neq \Gamma_m.$$

---

[6] $\Gamma_n{}^*$ is the irreducible representation whose matrices $D^n[R]^*$ are the complex conjugates of the matrices of Γ_n. If Γ_n is an irreducible representation then so is $\Gamma_n{}^*$, although if the $D^n[R]$ are real then $\Gamma_n \equiv \Gamma_n{}^*$.

As an example with imaginary characters, the character table of the $\boldsymbol{C}_3$ group is given in Table 6-4 and we see that

$$E_+^* \otimes E_+ = A_1 \tag{6-126}$$

but

$$E_+ \otimes E_+ = E_-, \tag{6-127}$$

since $\omega^* = \omega^2$ and $(\omega^2)^* = \omega$. Two representations (such as E_+ and E_- in $\boldsymbol{C}_3$) which have imaginary characters, and whose characters are the complex conjugates of each other, are said to be *separably degenerate* for reasons that we will appreciate in Chapter 7 when we discuss the operation of time reversal.

Table 6-4

The character table of the $\boldsymbol{C}_3$ group[a]

$\boldsymbol{C}_3$:	E	C_3	C_3^2
A_1:	1	1	1
E_+:	1	ω	ω^2
E_-:	1	ω^2	ω

[a] $\omega = \exp(2\pi i/3)$ and $\omega^3 = 1$.

6.5 THE USE OF SYMMETRY LABELS AND THE VANISHING INTEGRAL RULE

As a result of the discussion given after Eq. (6-61) we see that we can label molecular energy levels according to the irreducible representations of a symmetry group of the molecular Hamiltonian. The use of the symmetry labels that we put on energy levels is that they enable us to tell which of the levels can *interact* with each other as a result of adding some previously unconsidered term $\hat{H}'$ to the molecular Hamiltonian $\hat{H}^0$. The term $\hat{H}'$ may be part of the exact Hamiltonian that was ignored initially for convenience, or it may be the result of applying an external perturbation such as an electric or magnetic field or electromagnetic radiation.

Let us suppose that the Hamiltonian $\hat{H}^0$ ($\hat{H}'$ having been neglected) has normalized eigenfunctions Ψ_m^0 and Ψ_n^0, with eigenvalues E_m^0 and E_n^0, respectively, and that $\hat{H}^0$ commutes with the group of symmetry operations $\boldsymbol{G} = \{R_1, R_2, \ldots, R_h\}$. $\hat{H}^0$ will transform as the totally symmetric representation $\Gamma^{(s)}$ of $\boldsymbol{G}$, and we let Ψ_m^0, Ψ_n^0 and $\hat{H}'$ generate the representations Γ_m, Γ_n, and Γ' of $\boldsymbol{G}$, respectively. The complete set of eigenfunctions of $\hat{H}^0$ form a *basis set* for determining the eigenfunctions and eigenvalues of the Hamiltonian

$H = (H^0 + H')$, and we can define the *Hamiltonian matrix* $\boldsymbol{H}$ in this basis set to be a matrix with *matrix elements* H_{mn} given by the integrals

$$H_{mn} = \int \Psi_m^{0\,*}(H^0 + H')\Psi_n^0 d\tau_S = \delta_{mn} E_n^0 + H'_{mn}, \tag{6-128}$$

where

$$H'_{mn} = \int \Psi_m^{0\,*} H' \Psi_n^0 d\tau_S \tag{6-129}$$

and $d\tau_S$ is the volume element in the space of the coordinates $X_1, Y_1, Z_1, \ldots$ of the particles in the molecule (i.e., $d\tau_S = dX_1\, dY_1\, dZ_1 \cdots$). The eigenvalues E of H can be determined (as we will see in the next section) from the Hamiltonian matrix by solving the *secular equation*

$$|H_{mn} - \delta_{mn} E| = 0. \tag{6-130}$$

In solving the secular equation (this is called *diagonalizing* the Hamiltonian matrix) it is important to know which of the off-diagonal matrix elements H'_{mn} vanish since this will enable us to simplify the equation.

We can use the symmetry labels Γ_m and Γ_n on the levels E_m^0 and E_n^0, together with the symmetry Γ' of H', to determine which H'_{mn} elements must vanish. We write the integrand of H'_{mn} as

$$f(S) = \Psi_m^{0\,*} H' \Psi_n^0, \tag{6-131}$$

where S is a general point with coordinates $(X_1, Y_1, Z_1, \ldots)$. Suppose that the operation R_q of $\boldsymbol{G}$ moves S to a point S' with coordinates $(X'_1, Y'_1, Z'_1, \ldots)$; the volume element at S', $d\tau_{S'} = dX'_1\, dY'_1\, dZ'_1 \cdots$, must be equal to the volume element $d\tau_S$ at S for such a coordinate transformation. From Eqs. (1-18)-(1-19) we have

$$R_q f(S) = f(S') = f^{R_q}(S), \tag{6-132}$$

and since integration is carried out over all points S or S' (and since $d\tau_{S'} = d\tau_S$) we have

$$\int f(S) d\tau_S = \int f(S') d\tau_{S'} = \int f^{R_q}(S) d\tau_S = \int [R_q f(S)] d\tau_S. \tag{6-133}$$

Thus

$$h \int f(S) d\tau_S = \int \left[\sum_q R_q f(S)\right] d\tau_S, \tag{6-134}$$

where there are h operations R_q in the group $\boldsymbol{G}$ (i.e., the order of the group $\boldsymbol{G}$ is h). We can therefore write

$$H'_{mn} = \int \Psi_m^{0\,*} H' \Psi_n^0 d\tau_S = h^{-1} \int \left[\sum_q R_q(\Psi_m^{0\,*} H' \Psi_n^0)\right] d\tau_S. \tag{6-135}$$

We will use this equation to determine if H'_{mn} must vanish. The function $\Psi_m^{0\,*} H' \Psi_n^0$ generates the product representation $\Gamma_m{}^* \otimes \Gamma' \otimes \Gamma_n = \Gamma'_{mn}$ ($\Psi_m^{0\,*}$ has symmetry $\Gamma_m{}^*$), and we consider the situation in which this does not contain the totally symmetric representation $\Gamma^{(s)}$, i.e.,

$$\Gamma_m{}^* \otimes \Gamma' \otimes \Gamma_n \not\supset \Gamma^{(s)}. \tag{6-136}$$

The $\Gamma^{(s)}$ projection operator in the group $\boldsymbol{G}$ is [see Eq. (6-67)]

$$P^{\Gamma^{(s)}} = \frac{1}{h} \sum_q R_q, \tag{6-137}$$

and if Eq. (6-136) is satisfied then $\Gamma^{(s)}$ will not occur in $\Gamma_m{}^* \otimes \Gamma' \otimes \Gamma_n$ so that

$$P^{\Gamma^{(s)}}(\Psi_m^{0\,*} H' \Psi_n^0) = 0, \tag{6-138}$$

i.e.,

$$\sum_q R_q(\Psi_m^{0\,*} H' \Psi_n^0) = 0. \tag{6-139}$$

Combining Eqs. (6-139) and (6-135) we see that the integral H'_{mn} will vanish if Eq. (6-136) is satisfied, i.e., if Γ'_{mn} does not contain $\Gamma^{(s)}$. Thus

$$\int \Psi_m^{0\,*} H' \Psi_n^0 d\tau = 0$$

if

$$\Gamma_m{}^* \otimes \Gamma' \otimes \Gamma_n \not\supset \Gamma^{(s)}. \tag{6-140}$$

This is *the vanishing integral rule*. If H' is totally symmetric in $\boldsymbol{G}$ then H'_{mn} will vanish if

$$\Gamma_m{}^* \otimes \Gamma_n \not\supset \Gamma^{(s)}, \tag{6-141}$$

i.e., [from Eq. (6-125)], if

$$\Gamma_m \neq \Gamma_n. \tag{6-142}$$

It would be an accident if H'_{mn} vanishes although $\Gamma'_{mn} \supset \Gamma^{(s)}$, but see the footnote on page 100.

For an l_m-fold degenerate irreducible representation Γ_m the vanishing integral rule can be extended. The eigenfunctions of H^0 with Γ_m symmetry can be written as Ψ_{mt}^0, $t = 1, 2, 3, \ldots, l_m$. These functions transform irreducibly as given in Eq. (6-66), generating the $l_m \times l_m$ representation matrices $D^{\Gamma_m}[R]$. The function Ψ_{mt}^0 transforms as the t'th row of Γ_m. By an extension of the arguments given above [see, for example, Section 4-9 of Tinkham (1964)] it can be shown that if $\hat{H}'$ is totally symmetric in $\boldsymbol{G}$, the integral

$$\int \Psi_{mt}^{0}{}^{*} \hat{H}' \Psi_{mu}^{0} d\tau = 0 \tag{6-143}$$

if $t \neq u$. The vanishing integral rule states that matrix elements such as that in Eq. (6-143) will vanish unless Ψ_{mt}^0 and Ψ_{mu}^0 transform according to the same irreducible representation Γ_m. However, even when this condition is satisfied, the two functions must transform as the same row of Γ_m for the matrix element to be nonvanishing.

6.6 DIAGONALIZING THE HAMILTONIAN MATRIX

We will now consider the secular equation [Eq. (6-130)] in more detail and demonstrate the importance of the vanishing integral rule. The eigenfunctions Ψ_n^0 and eigenvalues E_n^0 of the Hamiltonian operator $\hat{H}^0$ in Eq. (6-128) are such that

$$\hat{H}^0 \Psi_n^0 = E_n^0 \Psi_n^0, \tag{6-144}$$

and eigenfunctions belonging to different eigenvalues must be orthogonal to each other. We choose the degenerate eigenfunctions so that they are mutually orthogonal and we assume that all functions are normalized. In these circumstances we can set up the Hamiltonian matrix $\boldsymbol{H}^0$ using the eigenfunctions Ψ^0, and the matrix elements will be given by (where we write the volume element simply as $d\tau$ here)

$$H_{mn}^0 = \int \Psi_m^0{}^{*} \hat{H}^0 \Psi_n^0 d\tau = \delta_{mn} E_n^0. \tag{6-145}$$

The $\boldsymbol{H}^0$ matrix is diagonal in the eigenfunctions Ψ^0 of $\hat{H}^0$, and the diagonal elements are the eigenvalues of $\hat{H}^0$.

Let us suppose that the Ψ^0 functions introduced above are not eigenfunctions of the Hamiltonian operator $\hat{H} = \hat{H}^0 + \hat{H}'$. This means that

$$\hat{H} \Psi_n^0 \neq \varepsilon \Psi_n^0, \tag{6-146}$$

where ε is a constant, but rather that

$$\hat{H}\left(\sum_n C_{jn} \Psi_n^0\right) = E_j \left(\sum_n C_{jn} \Psi_n^0\right), \tag{6-147}$$

where the Ψ^0 functions form a complete set of basis functions. We wish to solve the set of simultaneous differential equations, Eq. (6-147), involving all E_j to obtain the eigenvalues E_j and eigenfunctions

$$\Psi_j = \sum_n C_{jn} \Psi_n^0 \tag{6-148}$$

of the Hamiltonian $\hat{H}$. Multiplying Eq. (6-147) on the left by $\Psi_m^{0\,*}$ and integrating over configuration space we obtain

$$\sum_n C_{jn} H_{mn} = E_j \sum_n C_{jn} \int \Psi_m^{0\,*} \Psi_n^0 \, d\tau = E_j \sum_n C_{jn} \delta_{mn}, \tag{6-149}$$

where

$$H_{mn} = \int \Psi_m^{0\,*} \hat{H} \Psi_n^0 \, d\tau. \tag{6-150}$$

The matrix $\boldsymbol{H}$ with elements H_{mn} is *Hermitian* [see Table 5-1], i.e.,

$$H_{mn} = H_{nm}^*, \tag{6-151}$$

because $\hat{H}$ is a *Hermitian operator*. In general, an operator $\hat{O}$ is said to be Hermitian if

$$\int \Psi_i^* \hat{O} \Psi_j \, d\tau = \int \left(\hat{O}\Psi_i\right)^* \Psi_j \, d\tau \tag{6-152}$$

for all wavefunctions Ψ_i and Ψ_j. For $\hat{O} = \hat{H}$ we obviously obtain Eq. (6-151) from Eq. (6-152). It follows from the postulates of quantum mechanics that the operators representing real quantities such as energy and angular momentum are Hermitian.

As an aside we mention here that for an arbitrary operator $\hat{O}$, we define the *Hermitian conjugate operator* $\hat{O}^\dagger$ so that the equation

$$\int \Psi_i^* \hat{O}^\dagger \Psi_j \, d\tau = \int \left(\hat{O}\Psi_i\right)^* \Psi_j \, d\tau \tag{6-153}$$

is fulfilled for all wavefunctions Ψ_i and Ψ_j. This definition is such that the matrix of $(\hat{O}^\dagger)_{ij}$ elements is the Hermitian conjugate of the matrix of $\hat{O}_{ij}$ elements (see Table 5-1). For a Hermitian operator $\hat{O}$ we have $\hat{O}^\dagger = \hat{O}$ from Eq. (6-152). It is left as an exercise for the reader to show that if $\hat{A}$ and $\hat{B}$ are two Hermitian operators that do not commute (i.e., the commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$), then the operators $\hat{A}\hat{B}$ and $\hat{B}\hat{A}$ are not Hermitian, but instead $(\hat{A}\hat{B})^\dagger = \hat{B}\hat{A}$ and $(\hat{B}\hat{A})^\dagger = \hat{A}\hat{B}$; however, $\hat{A}\hat{B} + \hat{B}\hat{A}$ is Hermitian. From Eq. (6-153) we can write

$$\int \left(\hat{O}\Psi_i\right)^* \hat{O}\Psi_j \, d\tau = \int \Psi_i^* \hat{O}^\dagger \hat{O} \Psi_j \, d\tau. \tag{6-154}$$

If $\hat{O}^\dagger \hat{O}$ is the identity operator then $\hat{O}$ is said to be *unitary* (see Table 5-1 for the definition of a unitary matrix) and we can write

$$\int \left(\hat{O}\Psi_i\right)^* \hat{O}\Psi_j \, d\tau = \int \Psi_i^* \Psi_j \, d\tau. \tag{6-155}$$

However, if $\hat{O}$ is such that

$$\int \left(\hat{O}\Psi_i\right)^* \hat{O}\Psi_j \, d\tau = \left(\int \Psi_i^* \Psi_j \, d\tau\right)^* = \int \Psi_j^* \Psi_i \, d\tau, \tag{6-156}$$

then $\hat{O}$ is said to be *antiunitary*. The product of an antiunitary operator and a unitary operator has to be antiunitary, and the product of two antiunitary operators has to be unitary. It is easy to appreciate that the operation of complex conjugation, $\hat{K}$ say, is antiunitary since

$$\int \left(\hat{K}\Psi_i\right)^* \hat{K}\Psi_j \, d\tau = \int \Psi_i \Psi_j^* \, d\tau = \int \Psi_j^* \Psi_i \, d\tau. \tag{6-157}$$

The only symmetry operation we consider that is antiunitary is the time reversal operation (see Section 7.4).

Returning to Eq. (6-149); we rewrite it as

$$\sum_n (H_{mn} - \delta_{mn} E_j) C_{jn} = 0. \tag{6-158}$$

The matrix of elements C_{jn} is orthogonal (since the eigenfunctions Ψ_j are also required to be mutually orthogonal) so that $C_{jn} = (C^{-1})_{nj}$, and we can write Eq. (6-158) as the matrix product

$$\sum_n (H_{mn} - \delta_{mn} E_j)(C^{-1})_{nj} = 0. \tag{6-159}$$

Since the determinants of matrices [see Eq. (5-13)] multiply together in the same way as the matrices themselves we see that, apart from the useless solution of all $(C^{-1})_{nj}$ being zero, we obtain the solution of Eqs. (6-158) and (6-159) as the secular equation

$$|H_{mn} - \delta_{mn} E_j| = 0. \tag{6-160}$$

In general an l-dimensional Hamiltonian matrix leads to a secular equation with l eigenvalues. Substituting the eigenvalues E_j one at a time into Eq. (6-159) gives l simultaneous equations (as $m = 1$ to l) for the $(C^{-1})_{nj}$, and we obtain the elements in the jth column of the matrix C^{-1}. Since $(C^{-1})_{nj} = C_{jn}$ these coefficients form the jth row of the C matrix and are the coefficients of the basis functions Ψ_n^0 in the eigenfunction Ψ_j.

Let us introduce the diagonal matrix Λ where $\Lambda_{jj} = E_j$ and $\Lambda_{ij} = 0$ if $i \neq j$. Substituting this into Eq. (6-159) we obtain the equation

$$\sum_n H_{mn}(C^{-1})_{nj} = (C^{-1})_{mj} \Lambda_{jj} \tag{6-161}$$

which in matrix notation is

$$\boldsymbol{H}C^{-1} = C^{-1}\Lambda,$$

i.e.,

$$CHC^{-1} = \Lambda. \tag{6-162}$$

Thus the similarity transformation of the Hamiltonian matrix $\boldsymbol{H}$ using the matrix of eigenfunction coefficients C produces the diagonal matrix Λ of eigenvalues of $\boldsymbol{H}$.

The value of the vanishing integral theorem is that it allows the matrix $\boldsymbol{H}$ to be block diagonalized. This occurs if we order the eigenfunctions Ψ_n^0 according to their symmetry when we set up $\boldsymbol{H}$. Let us initially consider the case when $\Gamma' = \Gamma^{(s)}$. In this case all off-diagonal matrix elements between Ψ_n^0 basis functions of different symmetry will vanish, and the Hamiltonian matrix will block diagonalize with there being one block for each symmetry type of Ψ_n^0 function.[7] To diagonalize a block diagonal matrix according to Eq. (6-162) it follows from the definition of matrix multiplication that the C and C^{-1} matrices must be block diagonal in the same fashion. From the fact that the C matrix is block diagonal like the $\boldsymbol{H}$ matrix we see that each eigenfunction of $\hat{H}$ will only be a linear combination of Ψ_n^0 functions having the same symmetry in $\boldsymbol{G}$ ($\boldsymbol{G}$ being the symmetry group of $\hat{H}^0$). Thus the symmetry of each eigenfunction Ψ_j of $\hat{H}$ in the group $\boldsymbol{G}$ will be the same as the symmetry of the Ψ_n^0 basis functions that make it up ($\boldsymbol{G}$ is a symmetry group of $\hat{H}$ when $\Gamma' = \Gamma^{(s)}$), and each block of a block diagonal matrix can be diagonalized separately, which is a great simplification. The symmetry of the Ψ_j functions can be obtained from the symmetry of the Ψ_n^0 functions without worrying about the details of $\hat{H}'$ and this is frequently very useful. When $\Gamma' \neq \Gamma^{(s)}$ all off-diagonal matrix elements between Ψ^0 functions of symmetry Γ_m and Γ_n will vanish if Eq. (6-136) is satisfied, and there will also be a block diagonalization of $\boldsymbol{H}$ (it may be necessary to rearrange the rows and columns of $\boldsymbol{H}$, i.e., to rearrange the order of the Ψ_n^0 functions, to obtain $\boldsymbol{H}$ in block diagonal form). However, now nonvanishing matrix elements occur in $\boldsymbol{H}$ that connect Ψ_n^0 functions of different symmetry in $\boldsymbol{G}$, and as a result the eigenfunctions of $\hat{H}$ may not contain only functions of one symmetry type of $\boldsymbol{G}$; when $\Gamma' \neq \Gamma^{(s)}$ the group $\boldsymbol{G}$ is not a symmetry group of $\hat{H}$ and its eigenfunctions Ψ_j cannot be classified in $\boldsymbol{G}$. However, the classification of the basis functions Ψ_n^0 in $\boldsymbol{G}$ will still allow a simplification of the Hamiltonian matrix.

APPENDIX 6-1: PROOF THAT THE *D*[*R*] ARE REPRESENTATIONS

Consider two symmetry operations P_1 and P_2, and an l-fold degenerate energy level E_n with eigenfunctions $\Psi_{n1}, \Psi_{n2}, \ldots, \Psi_{nl}$. We can write [see

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[7] Because of Eq. (6-143) a block associated with an l_m-fold degenerate irreducible representation Γ_m will block diagonalize further into l_m sub-blocks, one for each row of Γ_m. Each of these l_m sub-blocks will have the same eigenvalues so it is sufficient to diagonalize only one of them. This additional block diagonalization will only be achieved if all sets of functions Ψ_{mt}^0 ($t = 1, 2, 3, \ldots, l_m$) belonging to Γ_m are chosen so that they generate the same representation matrices $D^{\Gamma_m}[R]$ [see Eq. (6-66)]. Such functions can be obtained by means of the projection operators described in Section 6.3.

Eqs. (1-18) and (1-19)]

$$P_2\Psi_{nk}(X_1, X_2, \ldots) = \Psi_{nk}(X_1', X_2', \ldots) = \Psi_{nk}^{P_2}(X_1, X_2, \ldots), \tag{6-163}$$

where

$$P_2 X_i = X_i'. \tag{6-164}$$

However $\Psi_{nk}^{P_2}(X_1, X_2, \ldots)$ is also an eigenfunction of $\hat{H}$ with eigenvalue E_n so we can write it as a linear combination of the initial l functions, i.e.,

$$\Psi_{nk}(X_1', X_2', \ldots) = \Psi_{nk}^{P_2}(X_1, X_2, \ldots) = \sum_{j=1}^{l} D[P_2]_{kj}\Psi_{nj}(X_1, X_2, \ldots). \tag{6-165}$$

Using these results we can write [see Eq. (1-43), for example]

$$\begin{aligned} P_1 P_2 \Psi_{ni}(X_1, X_2, \ldots) &= P_1\Psi_{ni}(X_1', X_2', \ldots) & \text{(6-166)}\\ &= \sum_{k=1}^{l} D[P_1]_{ik}\Psi_{nk}(X_1', X_2', \ldots) & \text{(6-167)}\\ &= \sum_{k=1}^{l} D[P_1]_{ik} \sum_{j=1}^{l} D[P_2]_{kj}\Psi_{nj}(X_1, X_2, \ldots) & \text{(6-168)}\\ &= \sum_{j=1}^{l}\sum_{k=1}^{l} D[P_1]_{ik} D[P_2]_{kj}\Psi_{nj}(X_1, X_2, \ldots). & \text{(6-169)} \end{aligned}$$

The operation P_{12} is also a symmetry operation, where

$$P_{12} = P_1 P_2, \tag{6-170}$$

so that

$$P_1 P_2\Psi_{ni}(X_1, X_2, \ldots) = P_{12}\Psi_{ni}(X_1, X_2, \ldots) = \sum_{j=1}^{l} D[P_{12}]_{ij}\Psi_{nj}(X_1, X_2, \ldots). \tag{6-171}$$

Equating the right hand sides of Eqs. (6-169) and (6-171) we have

$$D[P_{12}]_{ij} = \sum_{k=1}^{l} D[P_1]_{ik} D[P_2]_{kj}. \tag{6-172}$$

This means that the matrices D obtained in this way form a representation of the group. (If they are one-dimensional matrices this still holds, and a one-dimensional representation is obtained.) This is discussed further in the Bibliographical Notes at the end of this chapter.

APPENDIX 6-2: PROJECTION OPERATORS

We consider the r functions $\Phi_1, \ldots, \Phi_r$ that transform according to the reducible representation Γ which can be reduced to the sum of irreducible representations Γ_1, Γ_2, Γ_3, etc. Since Γ is reducible we can block diagonalize all its matrices $D^{\Gamma}[R]$ by the same similarity transformation, and we let the orthogonal $r \times r$ matrix required be A such that

$$AD^{\Gamma}[R]A^{-1} = D^{\Gamma_1}[R] \oplus D^{\Gamma_2}[R] \oplus D^{\Gamma_3}[R] \oplus \cdots, \tag{6-173}$$

where the right hand side of this equation is shorthand for an $r \times r$ matrix block diagonalized into irreducible blocks $D^{\Gamma_j}[R]$. The irreducible representation Γ_j is l_j-dimensional so that $D^{\Gamma_j}[R]$ is an $l_j \times l_j$ matrix. We assume that for each irreducible representation Γ_j, we have a set of l_j functions, Ψ_{jk}, $k = 1, 2, 3, \ldots, l_j$, which generate the matrices $D^{\Gamma_j}[R]$ as given by Eq. (6-66)

$$R\Psi_{jk} = \sum_{s=1}^{l_j} D^{\Gamma_j}[R]_{ks}\Psi_{js}. \tag{6-174}$$

Using Eqs. (6-54)-(6-61) we deduce that we can write each function Φ_n as a linear combination of functions Ψ_{jk}:

$$\Phi_n = \sum_j \sum_{k=1}^{l_j} A_{n,jk}\Psi_{jk}, \tag{6-175}$$

and the inverse is

$$\Psi_{jk} = \sum_n [A^{-1}]_{jk,n}\Phi_n. \tag{6-176}$$

The problem we face is: Given the r functions Φ_n transforming as the reducible representation Γ, how do we determine the linear combinations Ψ_{im} that transform irreducibly? In the remarks after Eq. (6-65) we stated that the projection operator $P^{\Gamma_i}_{mm}$ forms such a linear combination (or *projects out*) from Φ_n the Ψ_{im} function that belongs to the m'th row of Γ_i in that it transforms according to Eq. (6-174). We now show this. We write

$$P^{\Gamma_i}_{mm}\Phi_n = \frac{l_i}{h}\sum_R D^{\Gamma_i}[R]^*_{mm} R\Phi_n \tag{6-177}$$

$$= \frac{l_i}{h}\sum_R D^{\Gamma_i}[R]^*_{mm} R \sum_j \sum_{k=1}^{l_j} A_{n,jk}\Psi_{jk} \tag{6-178}$$

$$= \sum_j \sum_{k=1}^{l_j} A_{n,jk}\frac{l_i}{h}\sum_R D^{\Gamma_i}[R]^*_{mm} \sum_{s=1}^{l_j} D^{\Gamma_j}[R]_{ks}\Psi_{js} \tag{6-179}$$

$$= \sum_j \sum_{k=1}^{l_j} A_{n,jk}\sum_{s=1}^{l_j}\Psi_{js}\left[\frac{l_i}{h}\sum_R D^{\Gamma_i}[R]^*_{mm} D^{\Gamma_j}[R]_{ks}\right] \tag{6-180}$$

where Eq. (6-178) follows from Eq. (6-175), and Eq. (6-179) follows from Eq. (6-174). Substituting the orthogonality relation Eq. (5-40) into Eq. (6-180) we obtain

$$P^{\Gamma_i}_{mm}\Phi_n = A_{n,im}\Psi_{im}, \tag{6-181}$$

since the term in square brackets in Eq. (6-180) is equal to one when $i = j$ and $k = s = m$, and zero otherwise. That is, by applying the projection operator $P^{\Gamma_i}_{mm}$ to Φ_n we have produced a function that belongs to the m'th row of Γ_i. Note that if $A_{n,im} = 0$, so that there is no function belonging to the m'th row of Γ_i in the set of Ψ_{jk} functions to which Φ_n reduces, then

$$P^{\Gamma_i}_{mm}\Phi_n = 0. \tag{6-182}$$

Even when Γ contains Γ_i Eq. (6-182) can be true for some of the r functions Φ_n but if Γ does not contain Γ_i then Eq. (6-182) is true for *all* of the r functions Φ_n.

We will now try to apply the transfer operator $P^{\Gamma_i}_{mt}$ defined by Eq. (6-69) to the function Ψ_{im} which belongs to the m'th row of Γ_i. We have

$$\begin{aligned} P^{\Gamma_i}_{mt}\Psi_{im} &= \frac{l_i}{h}\sum_R D^{\Gamma_i}[R]^*_{mt} R\Psi_{im} \\ &= \frac{l_i}{h}\sum_R D^{\Gamma_i}[R]^*_{mt} \sum_{s=1}^{l_i} D^{\Gamma_i}[R]_{ms}\Psi_{is} \\ &= \sum_{s=1}^{l_i}\Psi_{is}\left[\frac{l_i}{h}\sum_R D^{\Gamma_i}[R]^*_{mt} D^{\Gamma_i}[R]_{ms}\right] \\ &= \Psi_{it}. \end{aligned} \tag{6-183}$$

We have used Eq. (6-174) together with the orthogonality relation Eq. (5-40). This is proof of Eq. (6-70).

APPENDIX 6-3: ADDENDUM TO PROBLEM 6-2

To determine the representation of $C_{3v}(\mathrm{M})$ generated by the functions $\Phi_1(E)$ and $\Phi_2(E)$ in Problem 6-2 we proceed as follows:

$$(123)\Phi_1(E) = (X_3 - X_1)/\sqrt{2}, \tag{6-184}$$

and we write

$$(X_3 - X_1)/\sqrt{2} = c_{11}\Phi_1(E) + c_{12}\Phi_2(E), \tag{6-185}$$

which can be solved to give

$$c_{11} = -1/2 \text{ and } c_{12} = \sqrt{3}/2 \tag{6-186}$$

As expected, $c_{11} = D^E[(123)]_{11}$, and $c_{11} = D^E[(123)]_{12}$, where the matrices $D^E[R]$ are given in Eq. (6-85). Similarly

$$(123)\Phi_2(E) = c_{21}\Phi_1(E) + c_{22}\Phi_2(E) \tag{6-187}$$

which gives

$$c_{21} = -\sqrt{3}/2 \qquad \text{and} \qquad c_{22} = -1/2. \tag{6-188}$$

so that, again as expected, $c_{21} = D^E[(123)]_{21}$, and $c_{22} = D^E[(123)]_{22}$. The character of the matrix of the c_{ij} [or of the $D^E[(123)]_{ij}$] generated by (123) is thus given by

$$\chi[(123)] = c_{11} + c_{22} = -1. \tag{6-189}$$

We similarly determine that for $[\Phi_1(E), \Phi_2(E)]$

$$(12)^*\Phi_1(E) = (-X_2 + X_1)/\sqrt{2} = \Phi_1(E), \tag{6-190}$$

and

$$(12)^*\Phi_2(E) = (-2X_3 + X_1 + X_2)/\sqrt{6} = -\Phi_2(E). \tag{6-191}$$

These transformation properties are in accordance with the matrix $D^E[(12)^*]$ given in Eq. (6-85). It is seen that

$$\chi[(12)^*] = 0, \tag{6-192}$$

so that the function pair $[\Phi_1(E), \Phi_2(E)]$ is indeed of E symmetry. We can determine the transformation properties of $[\Phi_1(E), \Phi_2(E)]$ under the remaining $\boldsymbol{C}_{3v}(\mathrm{M})$ operations (132), $(23)^*$ and $(13)^*$ by using the relations $(132) = (123)(123)$, $(23)^* = (12)^*\,(123)$, and $(13)^* = (12)^*\,(123)\,(123)$. It follows from Eq. (6-172) that we can construct the representation matrices for (132), $(23)^*$ and $(13)^*$ by forming the analogous products of the matrices $D^E[(123)]]$ and $D^E[(12)^*]$. Since the group Γ_3 is isomorphic to $\boldsymbol{C}_{3v}(\mathrm{M})$, the desired representation matrices must necessarily be those given in Eq. (6-85).

BIBLIOGRAPHICAL NOTES

Margenau and Murphy (1956). The postulates of quantum mechanics are discussed on pages 337-344, and these were used (see particularly page 338) in obtaining Eqs. (6-4)-(6-7) in this chapter. The effect of a coordinate transformation on a volume element [see Eq. (6-133) here in which $d\tau_S = d\tau_{S'}$] is described on pages 172-173. The technique adopted above [see Eq. (6-49) and Appendix 6-1] for obtaining a matrix representation follows the procedure used on page 563 [see Eqs. (15-24)-(15-28)]. Determinants are defined on page 302.

Hamermesh (1964). The symmetric and antisymmetric product of a representation are discussed on page 132, and projection operators are discussed on pages 111-113.

Wigner (1959). Projection operators are discussed on pages 112-118, and the proof that mutually orthogonal wavefunctions generate a unitary representation is given on page 111.

The technique used in Wigner's book to generate matrix representations is different from that used in the present book. Having defined the effect of the operation R on coordinates by $RX_i = X_i'$ in Eq. (11.18a) Wigner defines another operation P_R in Eq. (11.19) by $P_R f(X_i') = f(X_i)$. Thus Wigner introduces the group of operations P_R, which transform functions, as being distinct from the group of operations R which change the values of nuclear coordinates and the values of functions of them. The groups $\{P_R\}$ and $\{R\}$ are isomorphic. We choose to define the nuclear permutation operations as permuting nuclei *and* transforming functions according to Eq. (1-18). (See Bibliographical Notes to Chapter 1). Wigner generates representation matrices $D^{\mathrm{W}}[R]$ (W for Wigner) by using [see Eq. (11.23) in Wigner's book]

$$P_R \Psi_{ni} = \sum_j D^{\mathrm{W}}[R]_{ji} \Psi_{nj}$$

(note the order of the subscripts) where $D^{\mathrm{W}}[R]$ is the matrix representing the operation R in the group of R operations; compare this with Eq. (6-49) here. Using Wigner's convention projection and transfer operators are defined using

$$P^{\Gamma_i}_{mm} = \frac{l_i}{h} \sum_R D^{\Gamma_i}[R^{-1}]^*_{mm} R, \qquad (6\text{-}193)$$

and

$$P^{\Gamma_i}_{mt} = \frac{l_i}{h} \sum_R D^{\Gamma_i}[R^{-1}]^*_{tm} R, \qquad (6\text{-}194)$$

which should be compared with Eqs. (6-64) and (6-69).

Bunker and Howard (1983). This paper makes a detailed comparison of the way representation matrices are generated here [using Eq. (6-49)] and the way they are generated by Wigner (1959). It is shown that each method is consistent and correct within itself. As explained in the Bibliographical Notes of Chapter 1 the use of Wigner's technique for permutation operations demands that the permutation operations permute particles according to space fixed position labels which do not move when nuclei are permuted. Similarly for rotation operations, Wigner's method would be used for rotations about space fixed axes (which do not move when rotation operations are applied) whereas the method described here would be used for rotations about molecule fixed axes (which move when a rotation operation is applied).

7

The Molecular Hamiltonian and its Symmetry

The expression for the complete molecular Hamiltonian is given, and several groups of operations (involving translations, rotations, permutations and the inversion) that commute with the Hamiltonian are examined. The energy levels of the Hamiltonian can be symmetry labeled by using the irreducible representations of these groups. The symmetry labels are called true symmetry labels since they involve the use of true symmetry groups of the Hamiltonian. Time reversal symmetry is also discussed, and the concept of a near symmetry group is introduced. In the Bibliographical Notes recent research on the possible breakdown of the 'true' symmetries is summarized.

7.1 THE MOLECULAR HAMILTONIAN

We consider a molecule to be a collection of nuclei and electrons held together by certain forces and obeying the laws of quantum mechanics. A classical expression for the energy of the molecule can be derived, and the postulates of quantum mechanics used to obtain the appropriate quantum mechanical Hamiltonian and Schrödinger equation. The molecular Hamiltonian operator $\hat{H}$ involves the properties of each of the nuclei and electrons in the molecule. The properties occurring are

m_r	the mass of each particle ($m_r = m_e$ for electrons),
$C_r e$	the charge of each particle ($C_r = -1$ for electrons),
g and $\hat{s}_i$	the g-factor and spin of each electron i (giving the electron spin magnetic moments),
g_α and $\hat{I}_\alpha$	the g-factor and spin of each nucleus α (giving the nuclear spin magnetic moments),
$Q_{ab}^{(\alpha)}$	the components of the electric quadrupole moment of each nucleus α,

and the higher electric and magnetic moments of the nuclei (when present). To this list of particle properties we could add others such as the polarizability of each nucleus. The time-independent Schrödinger equation $\hat{H}\Phi = E\Phi$ provides a prescription, using the laws that describe the interaction forces between the particles, for getting the molecular energies E and wavefunctions Φ from the properties of the nuclei and electrons in the molecule. As well as the particle properties the Hamiltonian involves the coordinates $\boldsymbol{R}_r$, the linear momentum operators $\hat{\boldsymbol{P}}_r$, and the spin angular momentum operators ($\boldsymbol{s}_i$ and $\boldsymbol{I}_\alpha$) for all the particles in the molecule, and we write the Hamiltonian as

$$\hat{H} = \underbrace{(\hat{T}_{CM} + \hat{T}^0 + \hat{T}')}_{\hat{T}} + V + \hat{H}_{es} + \hat{H}_{hfs}. \tag{7-1}$$

We will now discuss the meaning of each of these terms.

We first look at the nonrelativistic kinetic energy operator T in the Hamiltonian. This operator is given by

$$\hat{T} = -\frac{\hbar^2}{2}\sum_{r=1}^{l}\frac{(\partial^2/\partial \mathrm{X}_r{}^2) + (\partial^2/\partial \mathrm{Y}_r{}^2) + (\partial^2/\partial \mathrm{Z}_r{}^2)}{m_r}, \tag{7-2}$$

where r runs over all the nuclei and electrons in the molecule (the total number of particles is l), and the coordinates are in an arbitrary space fixed (X, Y, Z) axis system. We introduce the (X, Y, Z) axis system with origin at the molecular center of mass, and parallel to the (X, Y, Z) axis system, so that

$$\mathrm{X}_r = X_r + \mathrm{X}_0, \tag{7-3}$$

$$\mathrm{Y}_r = Y_r + \mathrm{Y}_0, \tag{7-4}$$

and

$$\mathrm{Z}_r = Z_r + \mathrm{Z}_0, \tag{7-5}$$

where (X_0, Y_0, Z_0) are the coordinates of the molecular center of mass in the (X, Y, Z) axis system. To separate the translational kinetic energy in Eq. (7-2) we write $\hat{T}$ in terms of the $3l$ coordinates

$$\mathrm{X}_0, \mathrm{Y}_0, \mathrm{Z}_0, X_2, Y_2, Z_2, \ldots, X_l, Y_l, Z_l, \tag{7-6}$$

where we have eliminated X_1, Y_1, and Z_1 using

$$X_1 = -\frac{1}{m_1}\sum_{r=2}^{l} m_r X_r, \tag{7-7}$$

with similar equations for Y_1 and Z_1. To make the coordinate change we use the *chain rule*. To explain the chain rule we consider for convenience the coordinate change from the coordinates $(Q_1, Q_2, \ldots, Q_n)$ to the coordinates $(q_1, q_2, \ldots, q_n)$, where $q_i = f_i(Q_1, Q_2, \ldots, Q_n)$. For this coordinate change the chain rule gives

$$\frac{\partial}{\partial Q_j} = \sum_i \frac{\partial q_i}{\partial Q_j}\frac{\partial}{\partial q_i}, \tag{7-8}$$

and by further differentiation we deduce that

$$\frac{\partial^2}{\partial Q_j^2}=\sum_{k,i}\left(\frac{\partial q_k}{\partial Q_j}\right)\left(\frac{\partial q_i}{\partial Q_j}\right)\frac{\partial^2}{\partial q_k\partial q_i}+\sum_i\left(\frac{\partial^2 q_i}{\partial Q_j^2}\right)\frac{\partial}{\partial q_i}. \tag{7-9}$$

We use the chain rule in order to obtain $\hat{T}$ in the coordinates of Eq. (7-6) from the expression for $\hat{T}$ given in Eq. (7-2). We obtain the results that

$$\frac{\partial^2}{\partial \mathrm{X}_1{}^2}=\left(\frac{m_1}{M}\right)^2\left(\frac{\partial^2}{\partial \mathrm{X}_0{}^2}-2\sum_{s=2}^{l}\frac{\partial^2}{\partial \mathrm{X}_0\partial X_s}+\sum_{s,t=2}^{l}\frac{\partial^2}{\partial X_s\partial X_t}\right), \tag{7-10}$$

and for $r \neq 1$

$$\frac{\partial^2}{\partial \mathrm{X}_r{}^2}=\left(\frac{m_r}{M}\right)^2\left(\frac{\partial^2}{\partial \mathrm{X}_0{}^2}-2\sum_{s=2}^{l}\frac{\partial^2}{\partial \mathrm{X}_0\partial X_s}+\sum_{s,t=2}^{l}\frac{\partial^2}{\partial X_s\partial X_t}\right)$$
$$+2\left(\frac{m_r}{M}\right)\left(\frac{\partial^2}{\partial \mathrm{X}_0\partial X_r}-\sum_{s=2}^{l}\frac{\partial^2}{\partial X_r\partial X_s}\right)+\frac{\partial^2}{\partial X_r{}^2}, \tag{7-11}$$

where M is the total mass of all the electrons and nuclei in the molecule. Substituting Eqs. (7-10) and (7-11) and the similar equations for the Y and Z derivatives into Eq. (7-2) we obtain

$$\hat{T}=\hat{T}_{\mathrm{CM}}+\hat{T}^0+\hat{T}', \tag{7-12}$$

where

$$\hat{T}_{\mathrm{CM}}=-(\hbar^2/2M)\nabla^2_{\mathrm{CM}}, \tag{7-13}$$

$$\hat{T}^0=-(\hbar^2/2)\sum_{r=2}^{l}(\nabla_r^2/m_r), \tag{7-14}$$

$$\hat{T}'=(\hbar^2/2M)\sum_{r,s=2}^{l}\nabla_r\cdot\nabla_s, \tag{7-15}$$

$$\nabla^2_{\mathrm{CM}}=\partial^2/\partial \mathrm{X}_0{}^2+\partial^2/\partial \mathrm{Y}_0{}^2+\partial^2/\partial \mathrm{Z}_0{}^2, \tag{7-16}$$

$$\nabla_r{}^2=\partial^2/\partial X_r{}^2+\partial^2/\partial Y_r{}^2+\partial^2/\partial Z_r{}^2, \tag{7-17}$$

and

$$\nabla_r\cdot\nabla_s=\partial^2/\partial X_r\partial X_s+\partial^2/\partial Y_r\partial Y_s+\partial^2/\partial Z_r\partial Z_s. \tag{7-18}$$

Using $\hat{\boldsymbol{P}}_r=-i\hbar\partial/\partial\boldsymbol{R}_r$ we can introduce $\hat{\boldsymbol{P}}_r$ in place of the derivatives. The next term in the molecular Hamiltonian, Eq. (7-1), after the kinetic energy operator, is the electrostatic potential energy term V, and this is given by

$$V=\sum_{r<s=1}^{l}\frac{C_rC_se^2}{4\pi\epsilon_0R_{rs}}. \tag{7-19}$$

This term involves the interparticle distances R_{rs} [see Eq. (6-3)] and the electrostatic charges of the particles.

The term $\hat{H}_{\mathrm{es}}$ in the molecular Hamiltonian arises from the interaction of each of the electron spin magnetic moments with

(a) the magnetic moments generated by the orbital motions of the electrons (interaction with its own orbital motion is the most important and is called *the* electron spin–orbit interaction),

(b) the magnetic moments generated by the orbital motions of the nuclei, and

(c) the spin magnetic moments of the other electrons (the electron spin-spin interaction). The third term in Eq. (7-22) involves the Dirac delta function and represents a Fermi-contact-type interaction.

We write

$$\begin{aligned}
\hat{H}_{\mathrm{es}} &= \frac{g\mu_B}{4\pi\epsilon_0 m_e c^2}\sum_{j\neq i}(-e)R_{ij}^{-3}\left[(\boldsymbol{R}_i-\boldsymbol{R}_j)\times\left(\frac{\hat{\boldsymbol{P}}_i}{2}-\hat{\boldsymbol{P}}_j\right)\right]\cdot\hat{\boldsymbol{s}}_i && \text{(7-20)}\\
&+\frac{g\mu_B}{4\pi\epsilon_0 c^2}\sum_{\alpha,i}(C_\alpha e)R_{i\alpha}^{-3}\left[(\boldsymbol{R}_i-\boldsymbol{R}_\alpha)\times\left(\frac{\hat{\boldsymbol{P}}_i}{2m_e}-\frac{\hat{\boldsymbol{P}}_\alpha}{m_\alpha}\right)\right]\cdot\hat{\boldsymbol{s}}_i && \text{(7-21)}\\
&+\frac{g^2{\mu_B}^2}{4\pi\epsilon_0 c^2}\sum_{j>i}\Bigg\{(\hat{\boldsymbol{s}}_i\cdot\hat{\boldsymbol{s}}_j)R_{ij}^{-3}-3[\hat{\boldsymbol{s}}_i\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)][\hat{\boldsymbol{s}}_j\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)]R_{ij}^{-5}\\
&-\frac{8\pi}{3}\delta(\boldsymbol{R}_i-\boldsymbol{R}_j)(\hat{\boldsymbol{s}}_i\cdot\hat{\boldsymbol{s}}_j)\Bigg\}, && \text{(7-22)}
\end{aligned}$$

where α labels the nuclei, and i and j label the electrons; μ_B is the Bohr magneton ($\mu_B = \hbar e/2m_e$), and c is the speed of light.

$\hat{H}_{\mathrm{hfs}}$ is the last term that we consider in the molecular Hamiltonian and it results from the interactions of the magnetic and electric moments of the nuclei with the other electric and magnetic moments in the molecule. We call it the nuclear hyperfine structure term. Nuclei with spin 1/2 or greater have a nonvanishing magnetic dipole moment. The term $\hat{H}_{\mathrm{ns}}$, which is part of $\hat{H}_{\mathrm{hfs}}$ and which arises from the interaction of this nuclear spin magnetic moment with the other magnetic moments in the molecule, can be obtained from the expression for $\hat{H}_{\mathrm{es}}$ given above[1] by replacing the electron labels i and j by the nuclear labels α and β, replacing α by i, interchanging $-e$ and $C_\alpha e$, introducing $\hat{\boldsymbol{I}}_\alpha$ and $\hat{\boldsymbol{I}}_\beta$ instead of $\hat{\boldsymbol{s}}_i$ and $\hat{\boldsymbol{s}}_j$, introducing the nuclear g-factor g_α instead of g, and, finally, introducing $m_{\mathrm{p}}\mu_{\mathrm{N}}/m_\alpha$ instead of μ_{B} where μ_{N} is the nuclear magneton ($\mu_{\mathrm{N}} = \hbar e/2m_{\mathrm{p}}$ where m_{p} is the proton mass); both g_α and $1/m_\alpha$ must then be put inside the summation over α. Also included in $\hat{H}_{\mathrm{ns}}$ is the nuclear spin-electron spin coupling term, and this is analogous to Eq. (7-22). Nuclei with spin 1 or greater also have a nonvanishing electric quadrupole moment and nuclei with spin 3/2 or greater have a magnetic octupole moment as well; nuclei with higher spins can have even higher electric and magnetic moments. The electric moments arise from the non-spherical charge distribution over the finite volume of each nucleus, and the magnetic moments arise from the motions of the charges within each nucleus. All of these higher electric and magnetic moments interact with the charge distribution and charge motion within the molecule to give rise to further terms in $\hat{H}_{\mathrm{hfs}}$. Neglecting all but the quadrupole moment term $\hat{H}_{\mathrm{quad}}$ of these higher terms we can write the nuclear hyperfine term as

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[1] See Eq. (1) in Gunther-Mohr, Townes, and Van Vleck (1954).

$$\hat{H}_{\mathrm{hfs}} = \hat{H}_{\mathrm{ns}} + \hat{H}_{\mathrm{quad}}, \tag{7-23}$$

and

$$\hat{H}_{\mathrm{quad}} = -\frac{1}{6}\sum_{\alpha,a,b} Q_{ab}^{(\alpha)} V_{ab}^{(\alpha)}, \tag{7-24}$$

where the sum over α is over all nuclei and the sum over a and b is over the three molecule fixed coordinate directions; $Q_{ab}^{(\alpha)}$ is a component of the electric quadrupole moment of nucleus α, and $V_{ab}^{(\alpha)}$ is a component of the gradient of the electric field at nucleus α from all the other charges in the molecule. Nuclei with spin zero do not contribute to $\hat{H}_{\mathrm{hfs}}$ since such nuclei have no electric or magnetic moments. The effects of the terms $\hat{H}_{\mathrm{es}}$ and $\hat{H}_{\mathrm{hfs}}$ are discussed in Section 13.6.

The sum of the terms V, $\hat{H}_{\mathrm{es}}$ and $\hat{H}_{\mathrm{hfs}}$ describes the electromagnetic interactions between the particles.

From Eq. (7-1) we write the molecular Hamiltonian as

$$\hat{H} = \hat{T} + V + \hat{H}_{\mathrm{es}} + \hat{H}_{\mathrm{hfs}} \tag{7-25}$$

$$= \hat{T}_{\mathrm{CM}} + \hat{T}^0 + \hat{T}' + V + \hat{H}_{\mathrm{es}} + \hat{H}_{\mathrm{hfs}} \tag{7-26}$$

$$= \hat{T}_{\mathrm{CM}} + \hat{H}_{\mathrm{int}} \tag{7-27}$$

where $\hat{H}_{\mathrm{int}}$ is the Hamiltonian describing the internal dynamics of the molecule. The terms in $\hat{H}$ are summarized in Table 7-1.

We write the internal dynamics Hamiltonian as

$$\hat{H}_{\mathrm{int}} = \hat{H}_{\mathrm{rve}} + \hat{H}_{\mathrm{es}} + \hat{H}_{\mathrm{hfs}}, \tag{7-28}$$

where the spin-free rovibronic Hamiltonian $\hat{H}_{\mathrm{rve}}$ is

$$\hat{H}_{\mathrm{rve}} = \hat{T}^0 + \hat{T}' + V. \tag{7-29}$$

The rovibronic Schrödinger equation is given by

$$\hat{H}_{\mathrm{rve}}\Phi_{\mathrm{rve}} = E_{\mathrm{rve}}\Phi_{\mathrm{rve}}. \tag{7-30}$$

Table 7-1

The terms in the molecular Hamiltonian $\hat{H}$ given in Eq. (7-25)

$\hat{T}$	Kinetic energy	Eq. (7-2)
$\hat{T}_{\mathrm{CM}}$	Kinetic energy of the center of mass	Eq (7-13)
$\hat{T}^{0}$	Intramolecular kinetic energy	Eq. (7-14)
$\hat{T}'$	Cross terms in intramolecular kinetic energy	Eq. (7-15)
V	Electrostatic potential energy	Eq. (7-19)
$\hat{H}_{es}$	Interaction energy of the electron spin magnetic moments	
$\hat{H}_{so}$	Electron spin-electron orbit interaction	Eq. (7-20)
$\hat{H}_{sr}$	Electron spin-nuclear motion interaction	Eq. (7-21)
$\hat{H}_{ss}$	Electron spin-electron spin interaction	Eq. (7-22)
$\hat{H}_{hfs}$	Interaction energy of the nuclear magnetic and electric moments	Eq. (7-23)
$\hat{H}_{ns}$	Interaction energy of the nuclear spin magnetic moments	
$\hat{H}_{nso}$	Nuclear spin-electron orbit interaction	
$\hat{H}_{nsr}$	Nuclear spin-nuclear motion interaction	
$\hat{H}_{nss}$	Nuclear spin-nuclear spin interaction	
$\hat{H}_{nses}$	Nuclear spin-electron spin interaction	
$\hat{H}_{\mathrm{quad}}$	Interaction energy of the nuclear electric quadrupole moments with the electric field gradients	Eq. (7-24)

For applications to the study of the energy level spacings for singlet electronic ground states of molecules with unresolved nuclear hyperfine structure we can satisfactorily approximate $\hat{H}_{\mathrm{int}}$ by $\hat{H}_{\mathrm{rve}}$. For the general case we cannot make this approximation. However, the eigenstates of $\hat{H}_{\mathrm{rve}}$ are the starting point for any detailed calculation of molecular energies, and the neglected terms ($\hat{H}_{\mathrm{es}}$ and $\hat{H}_{\mathrm{hfs}}$) are treated as 'add-on' terms giving rise to energy level shifts, fine structure and hyperfine structure.

7.2 THE FULL SYMMETRY GROUP G_{FULL} OF THE MOLECULAR HAMILTONIAN

The complete molecular Hamiltonian $\hat{H}$ of Eq. (7-1) commutes with (or is invariant to) all of the following operations:

(a) any translation of the molecule along a space fixed direction,

(b) any rotation of the molecule about a space fixed axis passing through the center of mass of the molecule,

(c) any permutation of the space and spin coordinates of the electrons,

(d) any permutation of the space and spin coordinates of identical nuclei, and

(e) the inversion of the coordinates of all the particles (nuclei and electrons) in the center of mass of the molecule.

The invariance of $\hat{H}$ to these operations is not axiomatic but follows from the form of the Hamiltonian, and from the nature of space. The uniformity and isotropy of space is responsible for the symmetries (a) and (b) respectively. The indistinguishability of identical particles (electrons or nuclei) is responsible for the symmetries (c) and (d). The nature of the electromagnetic force is responsible for symmetry (e).

Before we discuss these five types of invariance in more detail it should be pointed out that we consider the molecule to be in the idealized circumstance of there being no intermolecular interactions and of there being no external fields, i.e., an isolated molecule in free space. We will not keep repeating 'for an isolated molecule in free space' below when we talk about the various symmetry operations but it will be understood.

Notice that in the above list of symmetry operations the operations of the molecular point group (i.e., rotations and reflections of the vibronic variables in the molecule fixed axis system) do not appear. The reason for this is that these operations do not commute with the complete molecular Hamiltonian; the molecular point group is a symmetry group of the vibronic Hamiltonian but not of the complete molecular Hamiltonian.

7.2.1 Active and passive transformations

The operations (a) and (b) above are described using the so-called *active* picture in which the operations are interpreted as involving a translation or rotation of the whole molecule within the space fixed reference frame. The effect of these operations on the Hamiltonian is exactly duplicated if we keep the molecule fixed and translate or rotate the space fixed axes in the opposite sense; this latter way of interpreting the effect of the operations is called the *passive* picture, and it leads to a clearer understanding of the invariance of the Hamiltonian. For example, instead of moving all the particles so that their spatial positions are changed from $\boldsymbol{R}_r$ to $\boldsymbol{R}_r + \boldsymbol{A}$ we could move the axes through $-\boldsymbol{A}$ when the same coordinate changes within the Hamiltonian will occur. It is immediately clear that a molecule is unaffected if we walk away from it, taking the space fixed axes with us, or if we walk around the molecule twisting the space fixed axes as we go. The molecular Hamiltonian must be invariant to all translations or rotations of the space fixed axis system. Hence the Hamiltonian is invariant to the translation or rotation of the molecule within the space fixed axis system.

7.3 SUBGROUPS OF THE G_{FULL} GROUP

The invariance of $\hat{H}$ to a translation of the molecule through $\boldsymbol{A}$, say (giving the direction and distance of the shift), results from the fact that $\hat{H}$ is unchanged if we add $\boldsymbol{A}$ to the position vectors of all particles in the molecule. The terms $\hat{T}_{\mathrm{CM}}$, $\hat{T}^0$, $\hat{T}'$, V, $\hat{H}_{\mathrm{es}}$, and $\hat{H}_{\mathrm{hfs}}$ are unchanged by the addition of $\boldsymbol{A}$ to the $\boldsymbol{R}_i$ and $\boldsymbol{R}_\alpha$, and the molecular Hamiltonian is therefore invariant to the translation through $\boldsymbol{A}$. Since $\boldsymbol{A}$ can be arbitrary the Hamiltonian is invariant to any translation and hence to all the elements of the translational group $\boldsymbol{G}_{\mathrm{T}}$. This is an infinite group consisting of all translations of the whole molecule by any amount along any direction in space.

The Hamiltonian is unchanged if we rotate the molecule about any space fixed axis passing through the center of mass of the molecule. Such an operation does not alter interparticle distances. As a result the molecular Hamiltonian is invariant to all the elements of the spatial three-dimensional pure rotation group $\boldsymbol{K}$(spatial) introduced in Chapter 4.

The molecular Hamiltonian is invariant to any permutation of the electrons. This operation merely involves interchanging the electron subscripts $i, j, k, \ldots$ on the vectors $\boldsymbol{R}$, $\hat{\boldsymbol{P}}$, and $\boldsymbol{s}$ in $\hat{H}$ where these vectors have the same coefficients (these coefficients involve the mass, charge, and g-factor of the electron). The invariance of $\hat{H}$ to a permutation of the electrons follows immediately from the fundamental fact that all the electrons in a molecule are identical and indistinguishable. The molecular Hamiltonian is therefore invariant to all the operations of the complete electron permutation group which we call $\boldsymbol{S}_{\mathrm{n}}^{(\mathrm{e})}$ (supposing there to be n electrons in the molecule). In the Bibliographical Notes the result of an experimental test for the indistinguishability of electrons is referenced.

In the same manner as the Hamiltonian is invariant to any permutation of electrons it is invariant to any permutation of identical nuclei. This just involves interchanging the nuclear labels on the quantities $\boldsymbol{R}$, $\hat{\boldsymbol{P}}$, $\hat{\boldsymbol{I}}$, Q_{ab}, and V_{ab}. This follows from the indistinguishability of identical nuclei. The Hamiltonian will therefore be invariant to the elements of the complete nuclear permutation group $\boldsymbol{G}^{\mathrm{CNP}}$ [see Eq. (1-56)]. Since electrons are fundamental particles, whereas nuclei are not, one can imagine that the indistinguishability of electrons is, in a sense, stronger than that of identical nuclei. This is discussed further in the Bibliographical Notes at the end of this chapter and at the end of Chapter 8.

The invariance of the molecular Hamiltonian to the inversion operation E^* requires examination. The effect of E^* is to change all position vectors $\boldsymbol{R}$ to $-\boldsymbol{R}$ and momentum vectors $\hat{\boldsymbol{P}}$ to $-\hat{\boldsymbol{P}}$ (these are polar vectors), within the (X, Y, Z) system, but not to change the spin vectors $\hat{\boldsymbol{I}}_\alpha$ and $\hat{\boldsymbol{s}}_i$ since they are axial vectors[2]. An axial vector transforms under E^* like the angular momentum vector $\boldsymbol{R} \times \hat{\boldsymbol{P}}$; since $\boldsymbol{R}$ and $\hat{\boldsymbol{P}}$ are reversed by E^* the vector product is invariant. The reader can see that, for example, $\hat{H}_{\mathrm{es}}$ and $\hat{H}_{\mathrm{ns}}$ are not altered if $\boldsymbol{R} \rightarrow$

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[2] **Polar and axial vectors are discussed, for example, on pages 164-165 in Margenau and Murphy (1956).**

$-\boldsymbol{R}, \boldsymbol{P} \rightarrow -\boldsymbol{P}, \boldsymbol{I} \rightarrow \boldsymbol{I}$ and $\boldsymbol{s} \rightarrow \boldsymbol{s}$. Examination of the electric quadrupole term in the Hamiltonian shows it to be invariant under E^* as are all terms that arise from intramolecular electromagnetic interactions. The above molecular Hamiltonian is invariant to the operation E^* and hence to the group $\mathcal{E} = \{E, E^*\}$. One should not be dogmatic about the invariance of the molecular Hamiltonian to E^*. The electromagnetic interaction force between nuclei and electrons in a molecule is invariant to inversion but the the weak interaction force is not. Hence if the contribution of the weak interaction force has to be considered then the term in the Hamiltonian that the effect contributes will not be invariant to E^*. This effect is very small indeed and in all normal spectroscopic work the effect of this possible term can certainly be neglected and the Hamiltonian taken as being invariant to E^*. This is discussed further in the Bibliographical Notes at the end of the chapter.

As a result of the above discussion we can take the molecular Hamiltonian as being invariant to the elements of the five groups $\boldsymbol{G}_{\mathrm{T}}$, $\boldsymbol{K}$(spatial), $\boldsymbol{S}_n^{(e)}$, $\boldsymbol{G}^{\mathrm{CNP}}$, and $\mathcal{E}$. Each of these groups is a true symmetry group of the molecular Hamiltonian. The full Hamiltonian group $\boldsymbol{G}_{\mathrm{FULL}}$ will therefore consist of the elements of each of these groups and of all possible products of the elements. Thus we can write $\boldsymbol{G}_{\mathrm{FULL}}$ as the direct product of these groups:

$$\boldsymbol{G}_{\mathrm{FULL}} = \boldsymbol{G}_{\mathrm{T}} \otimes \boldsymbol{K}(\text{spatial}) \otimes \boldsymbol{S}_n^{(e)} \otimes \boldsymbol{G}^{\mathrm{CNP}} \otimes \mathcal{E} \tag{7-31}$$

$$= \boldsymbol{G}_{\mathrm{T}} \otimes \boldsymbol{K}(\text{spatial}) \otimes \boldsymbol{S}_n^{(e)} \otimes \boldsymbol{G}^{\mathrm{CNPI}}, \tag{7-32}$$

where $\boldsymbol{G}^{\mathrm{CNPI}}$ is the complete nuclear permutation inversion group introduced in Chapter 2.

In Section 5.8.2 we describe how to obtain the irreducible representations of a direct product group $\boldsymbol{G} = \boldsymbol{A} \otimes \boldsymbol{B}$ from those of the invariant subgroups $\boldsymbol{A}$ and $\boldsymbol{B}$. These results can easily be generalized to a direct product of more than two subgroups [simply by assuming that $\boldsymbol{B}$, say, is a direct product, $\boldsymbol{B} = \boldsymbol{C} \otimes \boldsymbol{D}$]. It follows from these considerations, and from Eq. (7-32), that we can represent the irreducible representations of $\boldsymbol{G}_{\mathrm{FULL}}$, Γ_{FULL} say, as $(\Gamma_{\mathrm{T}}, \Gamma_{\mathrm{rot}}, \Gamma_n^{(e)}, \Gamma^{\mathrm{CNPI}})$, where Γ_{T}, Γ_{rot}, $\Gamma_n^{(e)}$, and Γ^{CNPI} are irreducible representations of the invariant subgroups $\boldsymbol{G}_{\mathrm{T}}$, $\boldsymbol{K}$(spatial), $\boldsymbol{S}_n^{(e)}$, and $\boldsymbol{G}^{\mathrm{CNPI}}$, respectively. From the results of Section 6.3.1 we see that the coordinates and wavefunctions transforming irreducibly in $\boldsymbol{G}_{\mathrm{FULL}}$ are those that simultaneously transform irreducibly in the four groups $\boldsymbol{G}_{\mathrm{T}}$, $\boldsymbol{K}$(spatial), $\boldsymbol{S}_n^{(e)}$, and $\boldsymbol{G}^{\mathrm{CNPI}}$. Consequently, in applications it is not necessary to use the complete group $\boldsymbol{G}_{\mathrm{FULL}}$, and the subgroups can be used separately.[3]

Symmetry labels (i.e., irreducible representation labels) obtained by using $\boldsymbol{G}_{\mathrm{FULL}}$ (or a subgroup of it) will be called true symmetry labels since they are obtained by using a group of elements that all commute with the exact molecular Hamiltonian. In particular the symmetry labels obtained by using the group $\boldsymbol{G}^{\mathrm{CNPI}}$ or the molecular symmetry group (a subgroup of $\boldsymbol{G}^{\mathrm{CNPI}}$; see

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[3] However, in the presence of an electric field a slightly different approach is necessary [see Section 14.5 and Watson (1975)].

Chapter 3) are true symmetry labels.

7.3.1 The translational group and linear momentum

The molecular Hamiltonian $\hat{H}$ [see Eq. (7-27)] can be written as

$$\hat{H} = \hat{T}_{\rm CM} + \hat{H}_{\rm int}, \tag{7-33}$$

where the internal Hamiltonian $\hat{H}_{\rm int}$ does not involve the coordinates (or momenta) of the molecular center of mass. Because of this separation of coordinates in the Hamiltonian we can write the eigenfunctions as

$$\Phi = \Phi_{\rm CM}({\rm X}_0, {\rm Y}_0, {\rm Z}_0)\Phi_{\rm int}(X_2, Y_2, Z_2, \ldots, X_l, Y_l, Z_l), \tag{7-34}$$

where

$$\hat{T}_{\rm CM}\Phi_{\rm CM} = E_{\rm CM}\Phi_{\rm CM}, \tag{7-35}$$

$$\hat{H}_{\rm int}\Phi_{\rm int} = E_{\rm int}\Phi_{\rm int}, \tag{7-36}$$

and the total energy is given without approximation by

$$E = E_{\rm CM} + E_{\rm int}. \tag{7-37}$$

Thus we can completely separate the translational motion from the internal motion. The translational wavefunction $\Phi_{\rm CM}$ is obtained from Eq (7-35) as

$$\Phi_{\rm CM} = e^{i\boldsymbol{k}\cdot\boldsymbol{R}_0}, \tag{7-38}$$

where $\boldsymbol{R}_0$ is the position vector of the center of mass [with components X$_0$, Y$_0$, and Z$_0$ in the (X, Y, Z) axis system], $\boldsymbol{k}\hbar = \boldsymbol{P}_{\rm CM}$ the classical translational momentum, and

$$k^2 = 2ME_{\rm CM}/\hbar^2. \tag{7-39}$$

A translational operation $R_{\rm T}$ which changes $\boldsymbol{R}_0$ to $\boldsymbol{R}_0 + \boldsymbol{A}$, say, will not affect $\Phi_{\rm int}$ and we can write

$$R_{\rm T}\Phi = R_{\rm T}\Phi_{\rm CM}\Phi_{\rm int} = \Phi_{\rm int}R_{\rm T}\Phi_{\rm CM}. \tag{7-40}$$

Thus to determine the effect of $R_{\rm T}$ on Φ we need only look at the effect of $R_{\rm T}$ on $\Phi_{\rm CM}$. From Eq. (7-38) we deduce that

$$R_{\rm T}\Phi_{\rm CM} = e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_0+\boldsymbol{A})} \tag{7-41}$$

$$= e^{i\boldsymbol{k}\cdot\boldsymbol{A}}\Phi_{\rm CM}, \tag{7-42}$$

so that the effect of a translational operation is determined solely by the $\boldsymbol{k}$ vector. Labeling the states according to the effect of the operations of $\boldsymbol{G}_{\mathrm{T}}$ is equivalent to labeling the states by the $\boldsymbol{k}$ vector (or translational momentum). The fact that $\boldsymbol{G}_{\mathrm{T}}$ commutes with the Hamiltonian means that there is conservation of linear momentum in an isolated molecule. We generally do not worry about the translational momentum of molecular states [except as it concerns the Doppler effect which causes line broadening; see, for example, Thorne (1974)]. When necessary, translational states are discussed by using the $\boldsymbol{k}$ vector and by using the law of conservation of momentum rather than by making explicit use of $\boldsymbol{G}_{\mathrm{T}}$. From now on we will neglect the molecular translational motion and concentrate on the complete internal motion Hamiltonian H_{int} and its eigenstates Φ_{int}.

7.3.2 The rotation group $\boldsymbol{K}$(spatial) and angular momentum

The group $\boldsymbol{K}$(spatial), introduced in Chapter 4, is an infinite (continuous) group with an infinite number of classes and therefore an infinite number of irreducible representations. In the same way that the transformation of Φ_{CM} under the effect of an operation of the group $\boldsymbol{G}_{\mathrm{T}}$ depends on the linear momentum of the state Φ_{CM} so the transformation of Φ_{int} under the effect of an operation of the group $\boldsymbol{K}$(spatial) depends on the angular momentum of the state Φ_{int}.

Each operation of the group $\boldsymbol{K}$(spatial) in the passive picture can be viewed as rotating the axes from (X, Y, Z) to a new orientation (X', Y', Z') and can be specified by the values of the three angles α, β, and γ in Fig. 7-1 that relate the orientation of (X', Y', Z') to that of (X, Y, Z). These angles are called Euler angles and they are restricted according to

$$0 \le \alpha \le 2\pi, \qquad 0 \le \beta \le \pi, \qquad 0 \le \gamma \le 2\pi. \tag{7-43}$$

The angles α and γ are measured in the positive (right handed) sense about the axes Z and Z', respectively. The angle γ is measured from the positive half of the node line ON which marks the intersection of the X, Y and X', Y' planes. The positive sense of ON is defined so that on rotating a right handed

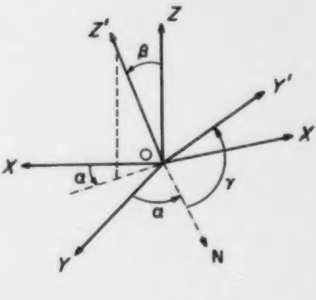

Fig. 7-1. The definition of the Euler angles (α, β, γ) that relate the orientation of the (X', Y', Z') axis system to that of the (X, Y, Z) axis system.

screw from Z to Z' through the angle β the screw travels in the positive sense along ON. Any operation of the group $\boldsymbol{K}$(spatial) can be written as $[\alpha, \beta, \gamma]$ and this notation specifies completely the axis rotation that results from application of the operation. One must be careful to specify whether one is using the active or passive picture of the rotation operation in explicitly writing down the effect of the operation.

The irreducible representations of the group $\boldsymbol{K}$(spatial) are written $D^{(0)}$ (the totally symmetric representation), $D^{(1)}$, $D^{(2)}$, etc., and in general we write $D^{(F)}$ where F is an integer;[4] the dimension of each matrix in the representation $D^{(F)}$ is $(2F + 1)$. We label the rows and columns of each matrix with m' and m respectively, where m' and $m = -F, -F+1, \ldots, +F$. The analytical expression for the elements $D^{(F)}_{m'm}(\alpha, \beta, \gamma)$ depends on whether the active or passive picture is used. Using the active picture (in which the functions are rotated) the expression is as given in Eq. (15.27) in Wigner (1959). To obtain the expression appropriate in the passive picture (in which the axes are rotated) one should change the signs of the three angles (α, β and γ) in Wigner's expression; the expression appropriate for the passive picture is also given by substituting Eq. (3.57) into Eq. (3.54) in Zare (1988) with ϕ, θ and χ replaced by α, β and γ respectively. More discussion of this point is given in the Bibliographical Notes at the end of the chapter.

The product of two representations of $\boldsymbol{K}$(spatial) is given by the following rule [see, for example, Section 6 'The Vector Addition Model' in Chapter 17 of Wigner (1959)]:

$$D^{(F_1)} \otimes D^{(F_2)} = D^{(F_1+F_2)} \oplus D^{(F_1+F_2-1)} \oplus \cdots \oplus D^{(|F_1-F_2|)}. \tag{7-44}$$

Extending this we can write the product of three representations as

$$\begin{aligned} &D^{(F_1)} \otimes D^{(F_2)} \otimes D^{(F_3)} \\ &\quad = D^{(F_1+F_2+F_3)} \oplus D^{(F_1+F_2+F_3-1)} \oplus \cdots \oplus D^{(|(F_1+F_2)-F_3|)} \\ &\quad\quad \oplus D^{(F_1+F_2-1+F_3)} \otimes D^{(F_1+F_2-1+F_3-1)} \oplus \cdots \oplus D^{(|(F_1+F_2-1)-F_3|)} \\ &\quad\quad \oplus \cdots \\ &\quad\quad \oplus D^{(|F_1-F_2|+F_3)} \oplus D^{(|F_1-F_2|+F_3-1)} \oplus \cdots \oplus D^{(||F_1-F_2|-F_3|)}. \end{aligned} \tag{7-45}$$

For example

$$\begin{aligned} D^{(1)} \otimes D^{(1)} \otimes D^{(2)} &= (D^{(2)} \oplus D^{(1)} \oplus D^{(0)}) \otimes D^{(2)} \\ &= D^{(4)} \oplus D^{(3)} \oplus D^{(2)} \oplus D^{(1)} \oplus D^{(0)} \\ &\quad \oplus D^{(3)} \oplus D^{(2)} \oplus D^{(1)} \\ &\quad \oplus D^{(2)}. \end{aligned} \tag{7-46}$$

In using the group $\boldsymbol{K}$(spatial) with the vanishing integral rule, Eq. (6-140), it is important to know that

$$D^{(F'')} \otimes D^{(1)} \otimes D^{(F')} \supset D^{(0)} \tag{7-47}$$

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[4] Half integral F will be considered in Chapter 18.

is only true if $F'' = F'$ (except $F' = F'' = 0$) or $F'' = F' \pm 1$.

As mentioned above the angular momentum associated with a molecular state is intimately related to the transformation properties of the molecular wavefunction in the group $\boldsymbol{K}$(spatial). Angular momentum will be discussed in more detail in Section 10.3, but a few words concerning its relation to symmetry in $\boldsymbol{K}$(spatial) are appropriate here. The molecular Hamiltonian $\hat{H}_{\mathrm{int}}$ commutes with the operators $\hat{\boldsymbol{F}}^2$ (the square of the total angular momentum, including the nuclear and electron spin angular momenta) and $\hat{F}_Z$ (a space fixed component of the total angular momentum) and so these quantities are conserved (like the energy E_{int} and the linear momentum $\boldsymbol{P}_{\mathrm{CM}}$) and do not change with time. We designate the value of the total angular momentum using the quantum number F, and the value of its space fixed projection using the quantum number m_F; we can indicate these quantum number values by writing the state function as $\Phi_{\mathrm{int}}(F, m_F)$. The connection between angular momentum and transformation properties in the group $\boldsymbol{K}$(spatial) is such that the molecular wavefunction $\Phi_{\mathrm{int}}(F, m_F)$ transforms in the group $\boldsymbol{K}$(spatial) according to the row labeled m_F in the representation $D^{(F)}$. Hence, the use of $\boldsymbol{K}$(spatial) to symmetry label the molecular wavefunctions is equivalent to labeling the states with the quantum numbers F and m_F.

The Hamiltonians $\hat{H}_{\mathrm{rves}}$ ($= \hat{H}_{\mathrm{rve}} + \hat{H}_{\mathrm{es}}$) and $\hat{H}_{\mathrm{rve}}$ [see Eq. (7-29)] each commute with the elements of the group $\boldsymbol{K}$(spatial) and with angular momentum operators. This means that we can introduce angular momentum quantum numbers for the the functions Φ_{rves} and Φ_{rve}. The notation for the angular momentum quantum numbers is such that we write $\Phi_{\mathrm{rves}}(J, m_J)$ and $\Phi_{\mathrm{rve}}(N, m)$. J is the quantum number for total angular momentum minus the nuclear spin angular momentum, and N is the quantum number for total angular momentum minus electron and nuclear spin angular momenta. This latter angular momentum (total minus spin angular momentum) is the ***rovibronic angular momentum***, and it is due to the orbiting motions of the nuclei and electrons in the molecule. For Φ_{rve} belonging to electronic singlet states (for which $J = N$) it is customary in the spectroscopic literature to use J rather than N as the rovibronic angular momentum quantum number.[5] This makes it difficult to avoid notational problems in some of the general rovibronic equations we develop later in the book. However, we try to use J as the rovibronic angular momentum quantum number for singlet states when possible, and when we feel it will not lead to confusion. Note that the rovibronic angular momentum $\hat{\boldsymbol{N}}$, and the angular momentum $\hat{\boldsymbol{J}}$ (the sum of $\hat{\boldsymbol{N}}$ and the electron spin angular momentum $\hat{\boldsymbol{S}}$), are not conserved quantities of the full Hamiltonian; see Section 13.6.

7.3.3 Fermi-Dirac and Bose-Einstein statistical formulas

Before considering the electron permutation group, or the complete nuclear permutation group, we introduce a law of nature concerning the effect of the permutation of identical particles. As discussed in Section 54 of Dirac (1958) any quantity of physical significance must be unaffected by the permutation of identical particles. One might say that the Hamiltonian of the universe commutes with any permutation of identical particles. Thus the permutational symmetry of each particle is a conserved quantity, and if a particular kind of particle starts out with a wavefunction that is symmetric with respect to exchange it will always remain so. Equally if it starts out being antisymmetric it will always remain so. In a non-relativistic theory this is as far as we can go, but by experiment it can be seen that there is a connection between the spin of a particle and the permutation symmetry of its wavefunctions.

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[5] This unfortunate convention is accepted by IUPAC; see Note (4) on p. 27 of Mills, Cvitaš, Homann, Kallay, and Kuchitsu (1993).

To discuss the relation between spin and permutational symmetry it is convenient to divide particles (i.e., nuclei and electrons) into two types: fermions, having half integer spin, and bosons, having integer spin. Thus electrons, protons, and ^{13}C, ^{11}B, and ^{17}O nuclei, for example, are fermions (having spins of $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$, respectively), and deuterons and ^{12}C, ^{10}B, and ^{16}O nuclei, for example, are bosons (having spins of 1, 0, 3, and 0; respectively).[6] The law of nature we introduce here is that any complete internal dynamics molecular wavefunction Φ_{int} is symmetric with respect to exchange of a pair of identical bosons in the molecule, but it is antisymmetric with respect to exchange of a pair of identical fermions in the molecule. Fermions are said to obey Fermi-Dirac statistical formulas and bosons to obey Bose-Einstein statistical formulas. The fact that the wavefunction is changed in sign by the permutation of a pair of identical fermions is called the *Pauli exclusion principle*; it results in the 'exclusion' of states that do not have this transformation property. It was first propounded by Pauli (1925) for electrons, and many years later Pauli (1940) was able to prove the general law for fermions and bosons using relativistic arguments. It is remarkable that a law of nature so simple to state should be so hard to prove. In his 1974 book *The Story of Spin*[7] Sin-itiro Tomonaga tells the tale of the pioneers of physics in their difficult journey towards an understanding of the nature of spin and its relationship to statistics.

The importance of these statistical formulas is that the complete internal wavefunctions Φ_{int} has to be invariant to any permutation of identical bosons in the molecule and to any even permutation of identical fermions, but will be changed in sign by an odd permutation of identical fermions. An even (odd) permutation can be expressed as an even (odd) number of successively applied pair transpositions (see Problem 1-4 on page 11).

7.3.4 The electron permutation group

In the group $S_n^{(e)}$ of order $n!$ there is one irreducible representation, $\Gamma^{(e)}(\mathrm{A})$ say, that has character $(+1)$ under all even permutations and (-1) under all odd permutations. Since electrons are fermions they obey Fermi-Dirac statistical formulas and the molecular wavefunction Φ_{int} must be changed in sign by an odd permutation of the electrons. Thus allowed Φ_{int} have to transform according to the representation $\Gamma^{(\mathrm{e})}(\mathrm{A})$ of $\boldsymbol{S}_n^{(\mathrm{e})}$. As a result all energy levels gain the same label $\Gamma^{(\mathrm{e})}(\mathrm{A})$ from the use of the group $\boldsymbol{S}_n^{(\mathrm{e})}$, and it would appear that this group is of no use in helping us either to distinguish between energy levels or to determine which energy levels can interact with one another.

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[6] Do any nuclei have spin 2?

[7] Now available translated into English by Prof. T. Oka [Tomonaga (1997)].

However, this group is of use when we combine electronic orbital (coordinate) functions and electronic spin functions in electronic structure calculations. The use of a Slater determinant (see Sections 9.4.2) as the form for an electronic basis function is a result of applying this symmetry. Using such basis functions [which have symmetry $\Gamma^{(\mathrm{e})}(\mathrm{A})$] ensures that the electronic wavefunctions finally obtained have symmetry $\Gamma^{(\mathrm{e})}(\mathrm{A})$ in the group $\boldsymbol{S}_n^{(\mathrm{e})}$ and thus satisfy the Pauli exclusion principle. In the symmetric group approach to electronic wavefunction calculations more extensive use is made of electron permutation groups (see Section 9.4.5).

One could imagine electronic orbital wavefunction calculations in which one did not worry about the Pauli exclusion principle. One would have to be careful when one combined the electronic spin states with such orbital functions in order to make sure that the Pauli exclusion principle were obeyed. For example, the ground electronic orbital wavefunction of the hydrogen molecule cannot be combined with a triplet electronic spin wavefunction; this would put two electrons in the same orbital state and in the same spin state. In this situation the electronic (spin and orbit) wavefunction would not change sign when the two electrons were permuted [it would not have $\Gamma^{(\mathrm{e})}(\mathrm{A})$ symmetry in the group $\boldsymbol{S}_2^{(\mathrm{e})}$, and thus it would violate the Pauli exclusion principle]. Such an electronic state is 'excluded' from existing by this symmetry rule. The ground electronic state of the hydrogen molecule has to be a singlet state and the use of this symmetry rule dictates the multiplicity of the state.

Notice that the nuclear (rotation-vibration) wavefunctions are unaffected by any electron permutation, and so these wavefunctions are not involved in the discussion of electron permutation symmetry. On the other hand electronic wavefunctions are transformed by the permutation of identical nuclei. This is because the molecule fixed (x, y, z) axes (which are introduced in Section 10.1.2) to which the electronic wavefunctions are referred are transformed by such permutations. Also LCAO electronic basis functions (see Section 9.4) are referred to numbered nuclei and transform when these nuclei are permuted. The transformation properties of the electronic wavefunctions under the effect of nuclear permutations will be discussed in Chapter 12.

7.3.5 The complete nuclear permutation group

In a molecule some of the nuclei may have integer spin and obey Bose-Einstein statistical formulas and some of the nuclei may have half integer spin and obey Fermi-Dirac statistical formulas. For the group $\boldsymbol{G}^{\mathrm{CNP}}$ of a particular isotopomer of a given molecule there will be one irreducible representation, which we call $\Gamma^{\mathrm{CNP}}(\mathrm{A})$, that has character $(+1)$ for all nuclear permutations except those that involve an odd permutation of fermion nuclei for which the character is (-1). From Bose-Einstein and Fermi-Dirac statistical formulas we deduce that the wavefunction Φ_{int} can only transform according to the representation $\Gamma^{\mathrm{CNP}}(\mathrm{A})$ of the group $\boldsymbol{G}^{\mathrm{CNP}}$. So this group appears to be of no use, as we initially thought about the $\boldsymbol{S}_n^{(\mathrm{e})}$ group.

We do not use the group $\boldsymbol{G}^{\mathrm{CNP}}$ in the way we used the $\boldsymbol{S}_n^{(\mathrm{e})}$ group. We do not set up appropriately combined rovibronic (rotation-vibration-electronic) and nuclear spin basis functions for solving the combined rovibronic and nuclear spin Hamiltonian. We rather follow the route suggested as a possible way to use the $\boldsymbol{S}_n^{(\mathrm{e})}$ group in the third paragraph of the above subsection. We solve the rovibronic problem without any regard for the statistical rules and then when we combine the rovibronic and nuclear spin wavefunctions we use the statistical rules to determine which combinations are allowed. This leads to the determination of the nuclear spin statistical weights which we discuss in the next chapter. This is essentially the same as the multiplicity restrictions that the Pauli exclusion principle imposes on the electronic states. However, it is slightly more complicated than the case with electrons since a molecule can contain several different types of nuclei having different spins. This, and the fact that electron spin fine structure is more important that nuclear hyperfine structure, are the reasons for the different approach.

7.3.6 The inversion group and parity

The group $\mathcal{E}$ has two representations which we call + or − depending on whether the character under E^* is +1 or −1. The wavefunction Φ_{int} can be + or − depending on the effect of E^* and we label the states with this parity label. The parity of a state (like its linear momentum, angular momentum, permutational symmetry and energy) is a conserved quantity and does not change with time. However, if we include the weak interaction force as a contributor to the forces between the particles in setting up the molecular Hamiltonian, as strictly speaking we should because of electroweak unification,[8] then the Hamiltonian will not commute with E^* and parity will then not be a conserved quantity. This effect is too small to have been seen yet in the study of molecules, but it has been seen in atoms (see the Bibliographical Notes). For all practical purposes in molecular spectroscopy we can ignore this symmetry breaking effect.

7.4 TIME REVERSAL SYMMETRY

In this section we will summarize material that is discussed at length in Chapter 26 of Wigner (1959), Chapter 15 of Abragam and Bleaney (1970), and

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[8] The unified treatment of electromagnetic and weak interaction forces which, within the Standard Model, satisfactorily describes all observed interparticle forces down to distances of the order of 10^{-16} cm.

Section 5-16 of Tinkham (1964). The time reversal operation $\hat{\theta}$ reverses all momenta ($\boldsymbol{P}$) including spin angular momenta ($\boldsymbol{s}$ and $\boldsymbol{I}$), but not the coordinates ($\boldsymbol{R}$), and it leaves the Hamiltonian invariant (for example, H_{es} and H_{ns} are invariant if $\boldsymbol{R} \rightarrow \boldsymbol{R}$, $\boldsymbol{P} \rightarrow -\boldsymbol{P}$, $\boldsymbol{I} \rightarrow -\boldsymbol{I}$, and $\boldsymbol{s} \rightarrow -\boldsymbol{s}$). The symmetry operation $\hat{\theta}$ has the effect of reversing the direction of motion and spin of the particles in the molecule. It is special in that it is antiunitary [as shown, for example, in Section 15.1 of Abragam and Bleaney (1970)], and this means that it has to be used slightly differently from the other (unitary) symmetry operations.

Unitary and antiunitary operators were defined in Eqs. (6-154)-(6-157), and it was shown that the operation of complex conjugation, called $\hat{K}$, is antiunitary. Since the product of two antiunitary operators is unitary the operation $\hat{O} = \hat{\theta}\hat{K}$ is unitary. Multiplying the equation $\hat{O}=\hat{\theta}\hat{K}$ on the right by $\hat{K}$, and using the fact that $\hat{K}^2 = 1$, we obtain the result that

$$\hat{\theta} = \hat{O}\hat{K}, \tag{7-48}$$

i.e., $\hat{\theta}$ is the product of a unitary operation and the complex conjugation operation. By squaring Eq. (7-48) we determine that

$$\hat{\theta}^2 = \pm 1. \tag{7-49}$$

It can be shown that [see, for example, Section 3.4 in Sachs (1987)]

$$\hat{\theta}\Phi_{\mathrm{int}}(F, m_F) = i^{2m_F}\Phi_{\mathrm{int}}(F, -m_F), \tag{7-50}$$

and, hence

$$\hat{\theta}^2\Phi_{\mathrm{int}}(F, m_F) = (-1)^{2m_F}\Phi_{\mathrm{int}}(F, m_F). \tag{7-51}$$

The quantum numbers F and m_F are half integral for molecules having an odd number of particles with half-integral spin, and integral for molecules having an even number of particles with half-integral spin. Thus $\hat{\theta}^2 = -1$ for molecules having an odd number of particles with half-integral spin, and +1 otherwise. In the former situation (in which one generally only considers the electrons although it has to also include nuclei having half-integral spin) the − sign leads to *Kramers' degeneracy* or *Kramers' theorem* [Kramers (1930)]. This states that all energy levels of a system containing an odd number of particles with half-integral spin must be at least doubly degenerate regardless of how low the (unitary) symmetry is. This follows from the fact that if $\hat{\theta}^2\Phi = -\Phi$ then it can be shown that $\hat{\theta}\Phi$ is orthogonal to Φ. Since $\hat{\theta}$ is a symmetry operation [see Eq. (6-19) and the remarks after it] $\hat{\theta}\Phi$ and Φ must have the same energy, they are orthogonal, and hence the level must be (at least) doubly degenerate. Kramers' degeneracy can only be lifted by an external magnetic field, and if nuclei with half-integral spin cause the degeneracy then one must resolve the nuclear hyperfine structure for the Kramers' degeneracy to be revealed.

Symmetry operations are either unitary or antiunitary, and all the symmetry operations we have dealt with so far are unitary except $\hat{\theta}$, and products of $\hat{\theta}$ with the unitary operations, which are antiunitary. The operation $\hat{\theta}$ will commute with all unitary operations of the symmetry group. In Chapters 5 and 6 we summarize the theory of representations and show how they are used to classify eigenfunctions of a Hamiltonian. The theory is presented with the (unstated) assumption that the symmetry operations are unitary. If we include the antiunitary operation $\hat{\theta}$ in the group, so that we now have a unitary-antiunitary symmetry group of the Hamiltonian, we can still use Eq. (6-49) to generate matrices for each operation in the group, and the matrices generated will be unitary because Eq. (6-62) will still apply. However, a matrix obtained in this way for an antiunitary operation will not, in general, multiply with the matrices obtained for the other operations in the group in the same way that the antiunitary operation itself multiplies with the other operations; hence the matrices will not form a representation of the group. Such a set of matrices is called a corepresentation of a unitary-antiunitary group [Wigner (1932,1959)]. In a corepresentation the unitary operations have a definite character (their matrices do multiply together in the same way as the unitary operations multiply together), but the characters under the antiunitary operations depend on the basis used to generate them. The properties of corepresentations are widely employed in the study of magnetic solids [see, for example, Dimmock and Wheeler (1964)], and they are equally applicable to molecules.

Table 7-2

The condensed character table of the C_3 group[a]

C_3 :	E	$C_3, C_3{}^2$	
A :	1	1	
E :	2	−1	sep

[a] The full character table is given in Table 6-4 on page 114, and the separably degenerate irreducible representations E_+ and E_- of that group are added to give E.

It turns out that including $\hat{\theta}$ in any symmetry group of the Hamiltonian, and then using corepresentations, does not lead to any new labels on the energy levels beyond that provided by the initial symmetry group (but see Chapter 18). For this reason this symmetry operation is usually ignored in molecular spectroscopy. However, the time reversal operation can provide extra information about whether matrix elements vanish in some circumstances [see, for example, Watson (1974) whose results are discussed further in Chapter 13 on page 386], and it can be responsible for extra degeneracies. If in the original symmetry group there is a pair of irreducible representations, Γ and Γ^*, say, that are the complex conjugates of each other then, as a result of time reversal symmetry, an energy level of symmetry Γ will always coincide with an energy level of symmetry Γ^* [see, for example, Hougen (1964b)]. For this reason such a pair of irreducible representations of a symmetry group can be considered to be degenerate and is called separably degenerate. The representations E_+ and E_- of the $\boldsymbol{C}_3$ group (see Table 6-4 on page 114) are separably degenerate. The character table of such a group can be condensed by adding the characters of each pair of separably degenerate irreducible representations, and such a condensed character table for the $\boldsymbol{C}_3$ group is given in Table 7-2. The operations C_3 and $C_3{}^2$ are not really in the same class but in the condensed character table that is how they appear. The fact that E is the sum of separably degenerate irreducible representations is indicated by writing 'sep' in the character table.

7.5 NEAR SYMMETRY

In the absence of external fields, the Hamiltonian H of an isolated molecule commutes with the elements of the molecular symmetry group of the molecule and with the elements of the group $\boldsymbol{K}$(spatial). Thus these two groups are true symmetry groups of H and we can label the molecular states according to the irreducible representations of these groups; such labels are called true symmetry labels. On the other hand a ***near symmetry group*** of H is such that its elements do not commute with H but rather they commute with an approximate Hamiltonian H^0; we can consider H^0 as being obtained from H by neglecting a small term H'. Writing

$$H = H^0 + H' \tag{7-52}$$

then for any element G of the near symmetry group

$$[G, H^0] = 0 \tag{7-53}$$

but

$$[G, H] = [G, (H^0 + H')] = [G, H'] \neq 0. \tag{7-54}$$

We can label the eigenstates of H^0 according to the irreducible representations of the near symmetry group [because Eq. (7-53) is true] and such labels will be useful ***near symmetry labels*** on the exact states (the eigenstates of H) if the symmetry breaking effects of H' are small. The term H' can mix eigenstates of H^0 that have different near symmetry labels (and hence break that symmetry) but, of course, it cannot mix states having different true symmetry labels [see the vanishing integral rule, Eq. (6-140)]. A symmetry group, and the symmetry labels obtained with it, are used to determine which of many possible terms in the Hamiltonian vanish and to determine which states are coupled by internally and externally caused perturbations. True symmetry groups give rigorously correct results. Near symmetry groups give rise to many more restrictions which, although only approximately true, usually enable us to understand the major perturbation effects. The near symmetry groups that we consider are ***molecular rotation groups*** and ***molecular point groups***. Their use is discussed in Chapters 12 and 13.

Table 7-3

The true symmetry groups of the Hamiltonian of an isolated molecule[a]

Fundamental property	Symmetry group	Symmetry operation[b]	Symmetry label[c]
Uniform space	Translation group $\boldsymbol{G}_{\mathrm{T}}$	Translation of the molecule along a space fixed direction	Linear momentum vector $\boldsymbol{k}$
Isotropic space	Spatial rotation group $\boldsymbol{K}$(spatial)	Rotation of the molecule about a space fixed axis	Angular momentum quantum numbers F, m_F
Indistinguishability of electrons	Electron permutation group $\boldsymbol{S}_n^{(e)}$	Permutation of the electrons	The antisymmetric representation $\Gamma^{(e)}(\mathrm{A})$
Indistinguishability of identical nuclei	Complete nuclear permutation group $\boldsymbol{G}^{\mathrm{CNP}}$	Permutation of the identical nuclei	The antisymmetric representation $\Gamma^{\mathrm{CNP}}(\mathrm{A})$
Conservation of parity[d]	Inversion group $\mathcal{E}$	Inversion of all particles through the molecular center of mass	Parity ±

[a] Time reversal symmetry is omitted.

[b] Using the active picture.

[c] The symmetry of the complete wavefunctions in $\boldsymbol{S}_n^{(e)}$ and $\boldsymbol{G}^{\mathrm{CNP}}$ is determined by Fermi-Dirac and Bose-Einstein statistical formulas to be $\Gamma^{(e)}(\mathrm{A})$ and $\Gamma^{\mathrm{CNP}}(\mathrm{A})$, respectively. See text.

[d] This is a property of the strong and electromagnetic interaction forces and it is not a property of the weak interaction force; it is not a property of space.

7.6 DISCUSSION

From the above considerations we see that we can label the translational states Φ_{CM} according to their linear momentum using $\boldsymbol{G}_{\mathrm{T}}$. The internal states Φ_{int} can be labeled with their angular momentum (F, m_F) using $\boldsymbol{K}$(spatial), and with their parity ($\pm$) using $\mathcal{E}$. The symmetry labels obtained by using the permutation groups are determined completely by the spin statistical formulas and all states $\Phi_{\rm int}$ for a particular molecule gain the same labels $[\Gamma^{(e)}({\rm A}), \Gamma^{\rm CNP}({\rm A})]$. The useful symmetry labels from $\boldsymbol{G}_{\rm FULL}$ on a molecular energy level, $E_{\rm int}$ (as opposed to the label on the wavefunction $\Phi_{\rm int}$), are $(F, \pm)$, and each level is $2F+1$ fold degenerate as $m_F = -F, -F+1, \ldots, +F$. The symmetry groups of the Hamiltonian of an isolated molecule in free space are summarized in Table 7-3.

In setting up electron spin–orbital basis functions to solve the electronic Hamiltonian we use a determinantal form that ensures that the Pauli exclusion principle is obeyed; this means that the final electronic states obtained will be properly symmetrized. This will be discussed in more detail in Section 9.4.2. When we solve the internal dynamics Hamiltonian we deal with the electronic, rotation-vibrational and nuclear spin parts separately. We then combine the electronic and rotation-vibration functions to determine the rovibronic states. The symmetrization of the final rovibronic-nuclear spin states gives the nuclear spin statistical weights as discussed in the next chapter. As a result the CNPI group and the $\boldsymbol{K}$(spatial) group become useful in labeling the basis functions and in determining which rovibronic interactions should be considered using the vanishing integral rule of Eq. (6-140). As explained in Chapter 3 we use the MS group rather than the CNPI group in applications; the group $\boldsymbol{K}$(spatial) is used separately to deal with angular momentum symmetry rules.

BIBLIOGRAPHICAL NOTES

The Hamiltonian

Moss (1973). Chapters 9 and 10 give a particularly useful account of the molecular Hamiltonian. Appendix A.2 explains how one can mindlessly convert equations expressed in the mixed CGS system to the corresponding SI equations.

Van Vleck (1951). Equation (37) and footnote 35.

Gunther-Mohr, Townes, and Van Vleck (1954). Equation (1).

The *K*(spatial) group

Wigner (1959). Chapter 15. Wigner uses the active picture in which the functions are rotated. The expression for the (active) $D^{(j)}_{\mu'\mu}(\alpha, \beta, \gamma)$ functions are given in Eq. (15.27).

Zare (1988). See Chapter 3 and particularly Sections 3.5 and 3.6. Zare uses the passive picture, in which the axes are rotated, in defining the analytical expressions for the functions $D^{(j)}_{m'm}(\alpha, \beta, \gamma)$ (where $\alpha\beta\gamma = \phi\theta\chi$; Zare uses the angles $\phi\theta\chi$). In Section 3.10 Zare relates the symmetric top rotational wavefunctions and the (passive) $D^{(j)}_{m'm}$ functions; we discuss this in Chapter 11 [see Eq. (11-13)].

Parity non-conservation

Parity non-conservation in an isolated molecule has not yet been observed, but it has been observed in a number of atoms. The experimental problem is to combine a highly sensitive and precise technique in circumstances where one can remove (or precisely account for) the effects of stray fields and intermolecular (or interatomic) interactions. The uncertainly in atomic theory calculations of the electronic wavefunction [1.2% for cesium. See Dzuba, Flambaum, and Sushkov (1989), and Blundell, Sapirstein and Johnson (1992)] is the current limiting factor in comparing the extent of the parity violation found by experiment to the predictions made using the Standard Model that unifies electromagnetic and weak interactions. The current measurements all fall within the predictions of the Standard Model when allowance is made for the uncertainties in the atomic theory calculations. Pages 122 to 128 of the book by Griffiths (1987) discusses parity, and the violation of parity conservation, in a very readable and instructive way. In the theoretical physics community the inversion symmetry operation is called P rather than E^*.

Wood, Bennett, Cho, Masterson, Roberts, Tanner and Wieman (1997). This experimental paper reports the measurement of the amplitude of the electric dipole component of the 6S to 7S transition in atomic cesium using a spin-polarized atomic beam. This electric-dipole transition is strictly forbidden by the parity selection rule but the weak neutral current interaction violates parity and mixes a small amount (about 10^{-11}) of the P state into the 6S and 7S states. The mixing results in a parity-violating electric-dipole transition amplitude that is nonvanishing. The measured transition amplitude is 1.5935 ± 0.0056 mV/cm.

Physics Today (1997). This *Search and Discovery* article discusses the results obtained in the above paper.

Haxton (1997). This *Perspectives* article also discusses the results obtained for cesium by Wood, Bennett, Cho, Masterson, Roberts, Tanner and Wieman (1997), particularly as it concerns the nuclear anapole moment.

The violation of the indistinguishability of 'identical' particles

Ramberg and Snow (1990). This experimental paper looks for a breakdown of the Pauli exclusion principle for electrons and fails to find it. In this experiment electrons are injected into a current carrying copper strip and a search is made for the X-rays that would be emitted if one of these electrons were captured by a copper atom and then cascaded down into the 1S state; the 1S level being already filled with two electrons. No such X-rays were found during a two month data collecting period in 1988. With a minimal set of assumptions the authors conclude that this implies that any violation of the Pauli exclusion principle is at a level of less than 1.7×10^{-26}; thus at this level the electrons are indistinguishable.

Physics Today (1996). This summarizes the situation concerning the (negative) experimental search for any violation of the Bose-Einstein statistical formulas for ^{16}O nuclei in the $^{16}O_2$ molecule. The experimental limit is at a level of around 10^{-6}, and thus at this level all ^{16}O nuclei are identical. This is further discussed in the Bibliographical Notes at the end of Chapter 8.

The violation of time reversal symmetry

Christenson, Cronin, Fitch and Turlay (1964). This is an experimental observation of the decay of the neutral K^0 meson. The result requires a violation of CP invariance, i.e., a violation of the invariance of the product of charge conjugation (C) and parity (P). Charge conjugation is the operation of converting every particle into its antiparticle and, like P-invariance, it is violated by weak interactions. It is believed that the combined operation of time reversal (called T here), charge conjugation and inversion in any order is an exact symmetry of any interaction, i.e., that is there is TCP invariance. As a result of TCP invariance a violation of CP invariance implies a violation of T-invariance. The decay of the neutral K^0 meson is the only known case of the violation of T-invariance and its origin is not understood; its extent cannot be calculated theoretically. Further it is impossible to construct a quantum field theory in which the product TCP is violated. If TCP violation were ever found it would be a monumental theoretical task to understand it. Pages 128 to 135 of Griffiths (1987) discusses CP and TCP violation.

Laerdahl, Saue, Fægri and Quiney (1997). This paper reports the results of making an *ab initio* calculation of PT-odd interactions in thallium fluoride.

8

Nuclear Spin Statistics

We begin by using the MS group to symmetry label the complete internal wavefunction and the nuclear spin wavefunctions. This provides a simple example of how one applies the MS group. It is shown how nuclear spin statistical weights arise, and we develop a formula that enables nuclear spin statistical weights to be determined easily. The concept of a 'missing' level is introduced. It is shown how useful it is to add the nuclear spin statistical weights to correlation tables and reverse correlation tables. The results presented here can be used to interpret the patterns that are found in the relative intensities of spectral lines (the so-called 'intensity alternations'). Such interpretations are often helpful in determining the equilibrium structure of a molecule, and in determining which tunneling motions produce observable splittings.

8.1 INTRODUCTION

In Section 7.3.3 we see that as a result of Fermi-Dirac and Bose-Einstein statistical formulas the symmetry of the complete internal wavefunction Φ_{int}, obtained after separating translation, is restricted. A rovibronic state (having symmetry Γ_{rve}) is only combined with a nuclear spin state (having symmetry Γ_{ns}), to form a basis function for expressing Φ_{int}, if the product of the two symmetries is an allowed symmetry for Φ_{int}. The number of nuclear spin states of each symmetry will, in general, differ and hence the number of nuclear spin states that can be combined with a given rovibronic state will differ depending on Γ_{rve}. This is the origin of nuclear spin statistical weights. It can happen that no nuclear spin state exists that has the right symmetry for combination with a particular rovibronic state and this rovibronic state will be *missing*. Such a rovibronic state is a perfectly acceptable eigenstate of the rovibronic Hamiltonian but it will not occur in nature because of this symmetry restriction.

8.2 THE CLASSIFICATION OF THE COMPLETE INTERNAL WAVEFUNCTION

8.2.1 Using the CNPI group

The complete internal wavefunction Φ_{int} can have + or − parity according to the effect of E^*, i.e.,

$$E^*\Phi_{\text{int}} = \pm\Phi_{\text{int}}. \tag{8-1}$$

Using the Fermi-Dirac and Bose-Einstein statistical formulas (see Section 7.3.3) we see that Φ_{int} is changed in sign by any nuclear permutation, $P_{(\text{odd})}$, that involves an odd permutation of nuclei that have half integer spin (fermions). This means that

$$P_{(\text{odd})}\Phi_{\text{int}} = -\Phi_{\text{int}}. \tag{8-2}$$

Alternatively Φ_{int} is invariant to a nuclear permutation, $P_{(\text{even})}$, that involves an even permutation of fermion nuclei regardless of whether the permutation involves an even or odd permutation of nuclei that have integer spin (bosons), i.e.,

$$P_{(\text{even})}\Phi_{\text{int}} = +\Phi_{\text{int}}. \tag{8-3}$$

Thus, for a particular isotopomer of a given molecule, Φ_{int} transforms as one of two nondegenerate irreducible representations of the CNPI group which we write as Γ^+ or Γ^- as the character is +1 or −1 under E^* (i.e., as the parity is + or −); the characters under the permutation operations are fixed by Eqs. (8-2) and (8-3).

We can use the H_2O and D_2O molecules as examples. For H_2O in its CNPI group $\boldsymbol{C}_{2v}(M)$ (see Table A-5) the operation (12) is an odd permutation of fermion nuclei and thus it changes the sign of Φ_{int}. As a result the symmetry of Φ_{int} is B_2 or B_1 as the parity is + or − (i.e., $\Gamma^+ = B_2$ and $\Gamma^- = B_1$ for H_2O). Since deuterium nuclei are bosons the operation (12) does not change the sign of Φ_{int} and the symmetry of the complete internal wavefunction of D_2O in $\boldsymbol{C}_{2v}(M)$ is A_1 or A_2 as the parity is + or − (i.e., $\Gamma^+ = A_1$ and $\Gamma^- = A_2$ for D_2O).

Problem 8-1. The CNPI groups of the molecules BF_3 and CH_4 are given in Tables A-10 and A-29, respectively. Determine the allowed symmetries of the complete internal wavefunctions of these molecules using Eqs. (8-1)-(8-3). Also determine the allowed symmetries for the complete internal wavefunction of CD_4, and the allowed symmetries of the complete internal wavefunctions of $^{12}C_2H_4$ and $^{13}C_2H_4$ in the CNPI group $\boldsymbol{G}_{96}$ (see Table 5-3).

Answer. For BF_3 since the fluorine nuclei are fermions, Φ_{int} is changed in sign by (23) but not by (123) [since (123) is an even permutation of the fluorine nuclei; see Eq. (1-26)]. Hence Φ_{int} has species A_2' or A_2'' in $\boldsymbol{D}_{3\text{h}}(\text{M})$ as the parity is + or −. For CH_4 the operations (23) and (1423) are odd permutations whereas (123) and (14)(23) are even so that Φ_{int} is of species A_2^+ or A_1^- in $\boldsymbol{G}_{48}$ as the parity is + or −. For CD_4 the complete internal species is A_1^+ or A_2^- as the parity is + or −. For $^{12}C_2H_4$ the species of the complete internal wavefunction is B_s^+ or B_s^- in $\boldsymbol{G}_{96}$ as the parity is + or −, and for $^{13}C_2H_4$ it is B_a^+ or B_a^- as the parity is + or −; ^{12}C nuclei are bosons and ^{13}C nuclei are fermions.

8.2.2 Using the MS group

In Chapter 3 we saw that a considerable simplification without loss of useful information is obtained by classifying the rovibronic wavefunctions in the MS group rather than in the CNPI group. When we do this we use rovibronic wavefunctions that are only evaluated over a small region of vibrational coordinate space; we denote such functions here as $\Phi_{\text{rve}}^{(l)}$ where (l) stands for *local*. For a rigid molecule, such as methane or methyl fluoride, the region of vibrational coordinate space considered only contains one version of the equilibrium structure, whereas for a molecule such as H_2O_2, in which observable tunneling effects occur, the region contains more than one version. For methane we have two parallel sets of rovibronic wavefunctions: $\Phi_{\text{rve}}^{(1A)}$ centered on configuration A [see Fig. 3-2a], and $\Phi_{\text{rve}}^{(1C)}$ centered on configuration C [see Fig. 3-2b]. Classifying one of these in the MS group provides a sufficient symmetry labeling of the energy levels. Similarly we need only consider local functions $\Phi_{\text{int}}^{(l)}$ and need only classify them in the MS group of the molecule rather than in the CNPI group.

The classification of $\Phi_{\text{int}}^{(l)}$ in the MS group is straightforward, and one could use the CNPI group → MS group correlation table to determine the species in the MS group to which the species $\Gamma^{\pm}$ correlate. For the methane molecule the species Φ_{int} in the CNPI group $\boldsymbol{G}_{48}$ can be either $\Gamma^+ = A_2^+$ or $\Gamma^- = A_1^-$. The correlation table of $\boldsymbol{G}_{48}$ to the MS group $\boldsymbol{T}_{\text{d}}(\text{M})$ yields the MS species A_2 or A_1, respectively, for levels that are A_2^+ or A_1^- in the CNPI group. Thus $\Phi_{\text{int}}^{(l)}$ functions of methane can have species A_1 or A_2 in the MS group. For $^{12}C_2H_4$ we have $\Gamma^+ = B_s^+$ and $\Gamma^- = B_s^-$ in $\boldsymbol{G}_{96}$, so that from Table 5-4 the $\Phi_{\text{int}}^{(l)}$ functions of the planar nontunneling molecule in the $\boldsymbol{D}_{2\text{h}}(\text{M})$ group can be A_g or A_u, respectively. Similarly for $^{13}C_2H_4$ we have $\Gamma^+ = B_a^+ \rightarrow B_{1u}$ in $\boldsymbol{D}_{2\text{h}}(\text{M})$ and $\Gamma^- = B_a^- \rightarrow B_{1g}$.

We use the notation Γ_{MS}^+ and Γ_{MS}^- for the two[1] allowed symmetry species of $\Phi_{\text{int}}^{(l)}$ in the MS group. Rather than determining the two allowed species of $\Phi_{\text{int}}^{(l)}$ in the MS group from the species in the CNPI group using the correlation table, we can determine them directly using the rules expressed in Eqs. (8-1) to (8-3), even if E^* is unfeasible. Both of these representations satisfy Eqs. (8-2) and (8-3) for the effect of a permutation; $\Gamma_{\text{MS}}^+(\Gamma_{\text{MS}}^-)$ has character $+1(-1)$ under

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[1] If no P^* operations are present $\Gamma_{\text{MS}}^+ = \Gamma_{\text{MS}}^-$.

$P^*_{(\mathrm{even})}$ and character $-1(+1)$ under $P^*_{(\mathrm{odd})}$, where $P^*_{(\mathrm{even})}$ is the product of E^* with an even permutation of fermion nuclei and $P^*_{(\mathrm{odd})}$ is the product of E^* with an odd permutation of fermion nuclei.

For example in $^{12}CH_4$, using the rules in Eqs. (8-2) and (8-3) with $\boldsymbol{T}_d(M)$ we determine from the characters under the permutation operations (123) and (14)(23), both of which are $P_{(\mathrm{even})}$ operations, that $\Phi^{(1)}_{\mathrm{int}}$ can only transform as $A_1 = \Gamma^+_{\mathrm{MS}}$ or $A_2 = \Gamma^-_{\mathrm{MS}}$. Similarly for $^{12}C_2H_4$ we see that $\Phi^{(1)}_{\mathrm{int}}$ can only be of symmetry $A_g = \Gamma^+_{\mathrm{MS}}$ or $A_u = \Gamma^-_{\mathrm{MS}}$ in $\boldsymbol{D}_{2h}(M)$ since these are the only two representations having character +1 for all the permutations [all the permutations in $\boldsymbol{D}_{2h}(M)$ are $P_{(\mathrm{even})}$ operations for $^{12}C_2H_4$]. For $^{13}C_2H_4$ the permutations (13)(24)(56) and (14)(23)(56) are odd permutations of fermions (the ^{13}C nuclei) and hence $\Phi^{(1)}_{\mathrm{int}}$ can only be $B_{1u} = \Gamma^+_{\mathrm{MS}}$ or $B_{1g} = \Gamma^-_{\mathrm{MS}}$.

For molecules whose MS group contains one or more permutation-inversion operations we always obtain two allowed species for the $\Phi^{(1)}_{\mathrm{int}}$ functions. For molecules whose MS group contains no permutation-inversion operations (and which are, therefore, optically active), such as CHIFCl or H_2S_2 with unfeasible internal rotation, the $\Phi^{(1)}_{\mathrm{int}}$ functions can only be of one species in the MS group and $\Gamma^+_{\mathrm{MS}} = \Gamma^-_{\mathrm{MS}}$. For example the complete internal wavefunction of $H_2{}^{32}S_2$ (^{32}S nuclei are bosons) must be changed in sign by the operation (12)(34) of the $\boldsymbol{C}_2(M)$ group (see Table A-4) and hence $\Phi^{(1)}_{\mathrm{int}}$ can only have species B in that group. The interpretation of this is appreciated if we look at the correlation of the species Γ^+ and Γ^- of the CNPI group to the species Γ^+_{MS} and Γ^-_{MS} in the MS group. If the MS group contains permutation-inversion operations then Γ^+ and Γ^- will correlate with the two different nondegenerate irreducible representation of the MS group that we call Γ^+_{MS} and Γ^-_{MS} respectively. If the MS group contains no permutation-inversion operations then Γ^+ and Γ^- will each correlate with the same nondegenerate irreducible representation of the MS group and each complete internal state of the molecule has a structural double degeneracy. Using Φ_{int} functions that are not local such a structural double degeneracy consists of a pair of states of opposite parity. For molecules with P^* operations in the MS group and for which two MS group species are obtained for $\Phi^{(1)}_{\mathrm{int}}$, we can identify one of the pair of species as correlating with a Φ_{int} state of + parity (this will have character +1 under $P^*_{(\mathrm{even})}$ operations) and the other as correlating with a Φ_{int} state of − parity (this will have character −1 under $P^*_{(\mathrm{even})}$ operations).

8.3 THE CLASSIFICATION OF THE NUCLEAR SPIN WAVEFUNCTIONS

For nucleus α having spin I_α the possible $(2I_\alpha + 1)$ nuclear spin functions can be written $|I_\alpha, m_{I_\alpha}\rangle$, where the projection quantum number m_{I_α} takes the values $-I_\alpha, -I_\alpha + 1, \ldots, +I_\alpha$. In a molecule containing N nuclei labeled 1, 2, …, N there will be a total of $(2I_1+1)(2I_2+1)\ldots(2I_N+1) = \prod(2I_i+1)$ nuclear spin functions. We wish to determine the representation of the MS group generated by this set of functions. One special property of spin functions is their invariance to E^*; they all have positive parity and hence the permutation-inversion operation $P^*=PE^*$ has the same effect on a nuclear spin function as the permutation P.

Before giving the equation for the characters in the representation generated by all the spin functions of a molecule we will work through an example. We will determine the species of the nuclear spin states of $^{14}NH_3$ in the MS group $\boldsymbol{D}_{3h}(M)$; the character table is given in Table A-10. For NH_3 we can construct the following proton spin functions, where α is the $|\frac{1}{2},\frac{1}{2}\rangle$ 'spin-up' nuclear spin function for a proton, and β is the $|\frac{1}{2},-\frac{1}{2}\rangle$ 'spin-down' function:

$$\begin{aligned}
(m_I = 3/2):&\quad \alpha\alpha\alpha = \Phi_{ns}^{(1)},\\
(m_I = 1/2):&\quad \alpha\alpha\beta = \Phi_{ns}^{(2)},\quad \alpha\beta\alpha = \Phi_{ns}^{(3)},\quad \beta\alpha\alpha = \Phi_{ns}^{(4)},\\
(m_I = -1/2):&\quad \alpha\beta\beta = \Phi_{ns}^{(5)},\quad \beta\alpha\beta = \Phi_{ns}^{(6)},\quad \beta\beta\alpha = \Phi_{ns}^{(7)},\\
(m_I = -3/2):&\quad \beta\beta\beta = \Phi_{ns}^{(8)},
\end{aligned} \tag{8-4}$$

where the nuclei are in the order 1, 2, and 3 in these functions, and $m_I = m_1 + m_2 + m_3$ is the total projection quantum number for the proton spins. Clearly both $\Phi_{ns}^{(1)}$ and $\Phi_{ns}^{(8)}$ are invariant to any operation of the group and have symmetry A_1'. The three $m_I = \frac{1}{2}$ spin functions are transformed amongst themselves by the elements of the group and the representation of $\boldsymbol{D}_{3h}(M)$ generated by these three functions is

$$\begin{matrix} E & (123) & (23) & E^* & (123)^* & (23)^* \\ 3 & 0 & 1 & 3 & 0 & 1 \end{matrix} \tag{8-5}$$

where the operations (23) and $(23)^*$ leave the function $\Phi_{ns}^{(4)}$ alone but interchanges the other two, and the operations (123) and $(123)^*$ permute all three functions. This representation reduces to the following irreducible representations of $\boldsymbol{D}_{3h}(M)$:

$$A_1' \oplus E'. \tag{8-6}$$

The three $m_I = -\frac{1}{2}$ spin functions generate the same representation of the MS group. Thus the representation generated by the eight proton spin functions is

$$4A_1' \oplus 2E', \tag{8-7}$$

and the characters are

$$\begin{matrix} E & (123) & (23) & E^* & (123)^* & (23)^* \\ 8 & 2 & 4 & 8 & 2 & 4 \end{matrix} \tag{8-8}$$

The three nuclear spin functions of the ^{14}N nucleus ($I = 1$, $m_I = -1$, 0 or +1) are each invariant to all of the elements of the MS group, and so the total representation generated by all 24 possible nuclear spin functions is simply obtained by multiplying Eq. (8-7) by three:

$$\Gamma^{\mathrm{tot}}_{\mathrm{nspin}} = 12A_1{}' \oplus 6E', \tag{8-9}$$

which has characters

$$\begin{array}{cccccc} E & (123) & (23) & E^* & (123)^* & (23)^* \\ 24 & 6 & 12 & 24 & 6 & 12 \end{array} \tag{8-10}$$

Each of the characters in this representation can be obtained directly [Landau and Lifshitz (1977)] by noticing that a contribution of +1 to the character is made if the permutation P (or permutation-inversion $P^* = PE^*$) permutes nuclei that have the same value of m_I, whereas if the nuclei have different values of m_I then one spin function is changed into another and no contribution to the character is made. We will use the effect of (23) to show how this observation can be made use of in developing a simple formula for the characters. We write a general nuclear spin function in $^{14}NH_3$ as $|\mathrm{spin}\rangle = |m_1, m_2, m_3, m_4\rangle$ where the N nucleus is labeled 4. There are $\prod(2I_i+1) = 24$ of these $|\mathrm{spin}\rangle$ functions and we want to determine how many of them are invariant to the operation (23); this will be the character under (23) in $\Gamma^{\mathrm{tot}}_{\mathrm{nspin}}$. Clearly all functions in which $m_2 = m_3$ will be invariant under (23) and they will be of two types: $|m_1, \frac{1}{2}, \frac{1}{2}, m_4\rangle$ or $|m_1, -\frac{1}{2}, -\frac{1}{2}, m_4\rangle$. The number of types is given by $(2I_2+1) = (2I_3+1) = 2$. For each of these types m_1 can be anything and there are $(2I_1+1) = 2$ possibilities for m_1. Also m_4 can be anything and there are $(2I_4+1) = 3$ possibilities for m_4. Thus the total number of functions that are left invariant is $(2I_2+1)$ times $(2I_1+1)(2I_4+1)$, i.e., 2×(2×3)=12. This is the character under (23) in $\Gamma^{\mathrm{tot}}_{\mathrm{nspin}}$. The general formula for the character $\chi^{\mathrm{tot}}_{\mathrm{nspin}}[P]$ under the permutation P (or permutation-inversion P^*) in $\Gamma^{\mathrm{tot}}_{\mathrm{nspin}}$ is thus:

$$\chi^{\mathrm{tot}}_{\mathrm{nspin}}[P] = \prod(2I_a+1), \tag{8-11}$$

where I_a is the nuclear spin, and the product contains one factor for each set of nuclei (including sets of one nucleus) permuted by P. For example, to apply this to $^{14}NH_3$ for $P = (23)$ we have three factors in the product: one for H_1, one for H_2 and H_3 taken together, and one for N:

$$\chi^{\mathrm{tot}}_{\mathrm{nspin}}[(23)] = [2\times(1/2)+1][2\times(1/2)+1][2\times 1+1] = 12. \tag{8-12}$$

To apply this for the operation (123) we have just two factors: one $[=(2\times\frac{1}{2}+1)]$ for H_1, H_2 and H_3, and one $[=(2\times1+1)]$ for N to give a total character of 6. For the operation E there is obviously one factor of $(2I+1)$ for each nucleus giving a character of $(2\times\frac{1}{2}+1)^3(2\times1+1)=24$.

The nuclear spin functions of $^{14}NH_3$ involve the total nuclear spin angular momentum quantum number I. Coupling the three proton spin angular momenta and the ^{14}N spin angular momentum, using Eq. (7-44) repeatedly, we obtain nuclear spin states having I = 5/2, 3/2 and 1/2 (giving 12 states of species $12A_1'$), and pairs of states having $I = 3/2$ and $1/2$ (giving 12 states of species $6E'$).

For ND_3 each deuterium nucleus has $I = 1$ and there are $3^3 = 27$ deuteron spin functions to be combined with the three nitrogen spin functions giving 81 in all. Using Eq. (8-11) for E, (23) and (123) we deduce the characters

$$\begin{array}{cccccc} E & (123) & (23) & E^* & (123)^* & (23)^* \\ 81 & 9 & 27 & 81 & 9 & 27 \end{array} \tag{8-13}$$

which reduces to

$$\Gamma^{\text{tot}}_{\text{nspin}} = 30A_1' \oplus 3A_2' \oplus 24E'. \tag{8-14}$$

Problem 8-2. Determine the representations of the MS group $\boldsymbol{D}_{2h}(M)$ (see Table A-9) generated by the nuclear spin wavefunctions of $^{12}C_2H_4$.

Answer. Since ^{12}C nuclei have a spin of zero there is a single nuclear spin function for each. There are $2^4 = 16$ proton spin functions. Using Eq. (8-11) we deduce that the 16 nuclear spin functions generate the representation

$$\Gamma^{\text{tot}}_{\text{nspin}} = 7A_g \oplus 3B_{3g} \oplus 3B_{1u} \oplus 3B_{2u}. \tag{8-15}$$

In the answer to Problem 8-2 we have determined the symmetry species of the 16 nuclear spin functions of $^{12}C_2H_4$ in the $\boldsymbol{D}_{2h}(M)$ group. We can equally well classify these functions in the $\boldsymbol{G}_{16}$ group appropriate if internal rotation splittings are resolved or even in the CNPI group $\boldsymbol{G}_{96}$ if we wish. The results are (see Table A-25)[2]

$$\Gamma^{\text{tot}}_{\text{nspin}}(\boldsymbol{G}_{16}) = 6A_1^+ \oplus B_1^+ \oplus 3B_2^+ \oplus 3E^+ \tag{8-16}$$

and (see Table 5-3)

$$\Gamma^{\text{tot}}_{\text{nspin}}(\boldsymbol{G}_{96}) = 5A_s^+ \oplus 3F_s^+ \oplus E_s^+. \tag{8-17}$$

Although Eq. (8-16) is equally applicable to the dimers $(H_2)_2$ and $(H_2{}^{16}O)_2$, one should note that the Γ(LH) notation for the irreducible representations of $\boldsymbol{G}_{16}$ is customarily used for the water dimer [Dyke (1977), Coudert and Hougen (1988,1990)].

8.4 THE DETERMINATION OF THE STATISTICAL WEIGHTS

To form a valid basis wavefunction we can only combine a rovibronic state $\Phi^{(1)}_{\text{rve}}$ having symmetry Γ_{rve} in the MS group with a nuclear spin state having symmetry Γ_{nspin} in the MS group if the product of these symmetries contains

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[2] We use the Γ(MW) notation for the irreducible representations of $\boldsymbol{G}_{16}$ in applications to the ethylene molecule.

Γ_{int}, where Γ_{int} is a species for $\Phi^{(1)}_{\text{int}}$ allowed by the statistical formulas, i.e., we must have

$$\Gamma_{\text{rve}} \otimes \Gamma_{\text{nspin}} \supset \Gamma_{\text{int}}. \tag{8-18}$$

We will use the $^{12}C_2H_4$ ethylene molecule as an example of the application of this rule. The rovibronic states of ethylene can be classified according to the eight irreducible representations of the $\boldsymbol{D}_{2h}(\text{M})$ group. The nuclear spin states have the symmetries given in Eq. (8-15) and the complete internal wavefunction can only be of either A_g or A_u species. To determine the statistical weights it is convenient to construct a table such as is shown in Table 8-1. In this table we first complete column 1 with all possible Γ_{rve} and then put the pairs of possible Γ_{int} in column 3. We now determine which of the nuclear spin functions [from Eq. (8-15)] can be combined with each rovibronic function so that the product of the nuclear spin symmetry and rovibronic symmetry is A_g or A_u; those that combine with Γ_{rve} to give a complete internal species of A_g are put on the left of the semicolon in column 2, and those that combine to give a complete internal species of A_u are put on the right. In this manner column 2 in Table 8-1 under Γ_{nspin} is completed. The statistical weights can now be easily determined as the number of possible $\Phi^{(1)}_{\text{int}}$ of the acceptable symmetry species that can be obtained from each $\Phi^{(1)}_{\text{rve}}$ by combining with nuclear spin functions. Tables such as these show which nuclear spin states each rovibronic state can be combined with.

Table 8-1

The statistical weights of the rovibronic states of $^{12}C_2H_4$ in the $\boldsymbol{D}_{2h}(\text{M})$ group

Γ_{rve}	Γ_{nspin}	Γ_{int}	Statistical weight	Γ_{rve}	Γ_{nspin}	Γ_{int}	Statistical weight
A_g	$7A_g$;–	A_g; A_u	7	A_u	–;$7A_g$	A_g; A_u	7
B_{1g}	–;$3B_{1u}$	A_g; A_u	3	B_{1u}	$3B_{1u}$;–	A_g; A_u	3
B_{2g}	–;$3B_{2u}$	A_g; A_u	3	B_{2u}	$3B_{2u}$;–	A_g; A_u	3
B_{3g}	$3B_{3g}$;–	A_g; A_u	3	B_{3u}	–;$3B_{3g}$	A_g; A_u	3

In Tables 8-2 and 8-3 similar statistical weight tables for $^{12}C_2H_4$ using the groups $\boldsymbol{G}_{16}$ and $\boldsymbol{G}_{96}$ are given. In $\boldsymbol{G}_{96}$ all "a" rovibronic states have zero statistical weight (i.e., they are missing), since Γ_{nspin} and Γ_{int} must be "s," and these rovibronic states have been omitted from the table. To obtain these results the direct product tables of the species of the groups are needed, and these are given in Table 8-4 for[3] $\boldsymbol{G}_{16}$ and in Table 8-5 for $\boldsymbol{S}_4^{(H)}$, from which that for $\boldsymbol{G}_{96}$ is easily derived since the subscripts and superscripts multiply as follows:

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[3] This direct product table is correct for either the Γ(LH) or Γ(MW) notations for the irreducible representations of $\boldsymbol{G}_{16}$.

$$\mathrm{a} \otimes \mathrm{a} = \mathrm{s} \otimes \mathrm{s} = \mathrm{s}, \quad \mathrm{a} \otimes \mathrm{s} = \mathrm{a}, \quad + \otimes + = - \otimes - = +, \quad \text{and} \quad + \otimes - = -. \tag{8-19}$$

Table 8-2

The statistical weights of the rovibronic states of $^{12}C_2H_4$ in the $\boldsymbol{G}_{16}$ group[a]

Γ_{rve}	Γ_{nspin}	Γ_{int}	Statistical weight	Γ_{rve}	Γ_{nspin}	Γ_{int}	Statistical weight
$A_1{}^+$	$B_1{}^+$;–	$B_1{}^+; A_1{}^-$	1	$A_1{}^-$	–;$6A_1{}^+$	$B_1{}^+; A_1{}^-$	6
$A_2{}^+$	$3B_2{}^+$;–	$B_1{}^+; A_1{}^-$	3	$A_2{}^-$	–;–	$B_1{}^+; A_1{}^-$	0
$B_1{}^+$	$6A_1{}^+$;–	$B_1{}^+; A_1{}^-$	6	$B_1{}^-$	–;$B_1{}^+$	$B_1{}^+; A_1{}^-$	1
$B_2{}^+$	–;–	$B_1{}^+; A_1{}^-$	0	$B_2{}^-$	–;$3B_2{}^+$	$B_1{}^+; A_1{}^-$	3
E^+	$3E^+$;–	$B_1{}^+; A_1{}^-$	3	E^-	–;$3E^+$	$B_1{}^+; A_1{}^-$	3

[a] We use the Γ(MW) notation for the irreducible representations of $\boldsymbol{G}_{16}$ in applications to the ethylene molecule.

Table 8-3

The statistical weights of the rovibronic states of $^{12}C_2H_4$ in the $\boldsymbol{G}_{96}$ group

Γ_{rve}	Γ_{nspin}	Γ_{int}	Statistical weight	Γ_{rve}	Γ_{nspin}	Γ_{int}	Statistical weight
$A_s{}^+$	–;–	$B_s{}^+; B_s{}^-$	0	$A_s{}^-$	–;–	$B_s{}^+; B_s{}^-$	0
$B_s{}^+$	$5A_s{}^+$;–	$B_s{}^+; B_s{}^-$	5	$B_s{}^-$	–;$5A_s{}^+$	$B_s{}^+; B_s{}^-$	5
$E_s{}^+$	$E_s{}^+$;–	$B_s{}^+; B_s{}^-$	1	$E_s{}^-$	–;$E_s{}^+$	$B_s{}^+; B_s{}^-$	1
$F_s{}^+$	–;–	$B_s{}^+; B_s{}^-$	0	$F_s{}^-$	–;–	$B_s{}^+; B_s{}^-$	0
$G_s{}^+$	$3F_s^+$;–	$B_s{}^+; B_s{}^-$	3	$G_s{}^-$	–;$3F_s^+$	$B_s{}^+; B_s{}^-$	3

Table 8-4

The direct product table of
the irreducible representations of $\boldsymbol{G}_{16}$[a]

	A_1	A_2	B_1	B_2	E
A_1:	A_1	A_2	B_1	B_2	E
A_2:	A_2	A_1	B_2	B_1	E
B_1:	B_1	B_2	A_1	A_2	E
B_2:	B_2	B_1	A_2	A_1	E
E:	E	E	E	E	$A_1 \oplus A_2 \oplus B_1 \oplus B_2$

[a] We omit the + and – labels since $+\otimes+ = -\otimes- = +$, and $+ \otimes - = -$.

As a result of the facts that nuclear spin wavefunctions have positive parity and that the complete internal wavefunction can have positive or negative parity without restriction, we could determine the statistical weights of the levels of any molecule by using the *permutation subgroup* of the MS group. This is the subgroup obtained by deleting all permutation-inversion elements in the MS group. This is in fact the customary way of determining nuclear spin statistical weights for rigid nonlinear molecules although the group is misleadingly called "the rotational subgroup of the molecular point group." Since in studying a molecule we determine the symmetry of the rovibronic levels in the MS group it is expedient to continue using this symmetry in the determination of the statistical weights, and that is why we discuss the determination of the statistical weights using the MS group rather than its permutation subgroup.

Table 8-5

The direct product table of the irreducible representations of $\boldsymbol{S}_4$

	A	B	E	F	G
A:	A	B	E	F	G
B:	B	A	E	G	F
E:	E	E	$A \oplus B \oplus E$	$F \oplus G$	$F \oplus G$
F:	F	G	$F \oplus G$	$A \oplus E \oplus F \oplus G$	$B \oplus E \oplus F \oplus G$
G:	G	F	$F \oplus G$	$B \oplus E \oplus F \oplus G$	$A \oplus E \oplus F \oplus G$

8.4.1 A simple method for determining statistical weights

The technique discussed above for the determination of the statistical weights becomes laborious to apply as the number of identical nuclei and the order of the MS group increase. Fortunately there is an alternative method that is tractable and easy to use even for large molecules. This method allows one to directly determine the allowed rovibronic states and their weights. The title of this section may have encouraged the reader to omit reading the previous section. We hope not since we feel that the previous section gives the reader an understanding of where the statistical weights come from, and an appreciation of which nuclear spin states can be combined with a given rovibronic state.

We use the $^{14}NH_3$ ammonia molecule to illustrate what we are going to do here to obtain a simple formula for the statistical weights. As we showed in Eq. (8-9) the nuclear spin states of $^{14}NH_3$ span the representation

$$\Gamma_{\text{nspin}}^{\text{tot}} = 12A_1' \oplus 6E', \tag{8-20}$$

in its MS group $\boldsymbol{D}_{3\text{h}}(\text{M})$. From the Pauli exclusion principle the complete internal wavefunction can have either A_2' or A_2'' species. Following the procedure outlined in the preceding section we determine that the rovibronic (including inversion) levels have statistical weights as given in Table 8-6. We see that states of species A_1' and A_2'' have a statistical weight of zero and are missing. A succinct way of giving the statistical weights would be to say that the allowed rovibronic states span the representation

$$\Gamma_{\mathrm{rve}}^{\mathrm{sw}} = 12A_2' \oplus 12A_2'' \oplus 6E' \oplus 6E''. \tag{8-21}$$

where the superscript sw stands for statistical weight. This expression gives the allowed rovibronic states and the numerical coefficients are their statistical weights: any symmetry species from the MS group that is absent here corresponds to a missing rovibronic level. There is a simple way of determining the characters of the representation $\Gamma_{\mathrm{rve}}^{\mathrm{sw}}$ from the expression in Eq. (8-11) for the characters in the representation $\Gamma_{\mathrm{nspin}}^{\mathrm{tot}}$ generated by the nuclear spin functions. This simple method is from Section 105 of Landau and Lifshitz (1977) as corrected by Jonas (1989).

Table 8-6

Statistical weights of rovibronic states[a] of NH_3

Γ_{rve}	Statistical weight	Γ_{rve}	Statistical weight
A_1'	0	A_1''	0
A_2'	12	A_2''	12
E'	6	E''	6

[a] Inversion states are included.

From Eqs. (8-1)-(8-3), and the rest of Section 8.2, we see that the complete internal wavefunction can only have symmetry Γ_{MS}^{+} or Γ_{MS}^{-} in the MS group. The representation Γ_{MS}^{+} has character +1 under any even fermion permutation-inversion $P_{(\mathrm{even})}^{*}$ in the MS group, and character −1 under any odd fermion permutation-inversion $P_{(\mathrm{odd})}^{*}$ in the MS group. The representation Γ_{MS}^{-} has character −1 under any $P_{(\mathrm{even})}^{*}$, and character +1 under any $P_{(\mathrm{odd})}^{*}$. These two representations have the same character under permutations (+1 under even fermion permutations and −1 under odd fermion permutations). Thus the character in the representation $\Gamma_{\mathrm{rve}}^{\mathrm{sw}}$ can be written as the sum of two characters: one appropriate if the complete internal wavefunction transforms as Γ_{MS}^{+} in the MS group, and one if it transforms as Γ_{MS}^{-}. We call the former (which corresponds to positive parity for the complete internal state) $\chi_{\mathrm{rve}}^{\mathrm{sw}}[O]^{+}$, and the latter (which corresponds to negative parity for the complete internal state) $\chi_{\mathrm{rve}}^{\mathrm{sw}}[O]^{-}$, where O is any operation in the MS group. The character we seek is then written as the sum

$$\chi_{\mathrm{rve}}^{\mathrm{sw}}[O] = \chi_{\mathrm{rve}}^{\mathrm{sw}}[O]^{+} + \chi_{\mathrm{rve}}^{\mathrm{sw}}[O]^{-}. \tag{8-22}$$

If O is any nuclear permutation P operation in the MS group then

$$\chi_{\mathrm{rve}}^{\mathrm{sw}}[P]^{+} = \chi_{\mathrm{rve}}^{\mathrm{sw}}[P]^{-}. \tag{8-23}$$

since Γ^{+}_{MS} and Γ^{-}_{MS} have the same characters under a permutation operation. Thus we have

$$\chi^{\mathrm{sw}}_{\mathrm{rve}}[P] = 2\chi^{\mathrm{sw}}_{\mathrm{rve}}[P]^{+}. \tag{8-24}$$

However, the characters have opposite sign under any permutation-inversion operation P^* in the MS group and so we have

$$\chi^{\mathrm{sw}}_{\mathrm{rve}}[P^*]^{+} = -\chi^{\mathrm{sw}}_{\mathrm{rve}}[P^*]^{-}. \tag{8-25}$$

Thus for a permutation-inversion

$$\chi^{\mathrm{sw}}_{\mathrm{rve}}[P^*] = 0. \tag{8-26}$$

The character $\chi^{\mathrm{sw}}_{\mathrm{rve}}[P]^{+}$ will be the same as the character $\chi^{\mathrm{tot}}_{\mathrm{nspin}}[P]$ [see Eq. (8-11)] if P is an even permutation of fermion nuclei because the representations generated by the rovibronic and nuclear spin functions must multiply together to give a component with a +1 as the character under any $P_{(\mathrm{even})}$ operation (the complete internal wavefunction transforms like that). However, if P is an odd permutation of fermion nuclei the character $\chi^{\mathrm{sw}}_{\mathrm{rve}}[P]^{+}$ will be of opposite sign to the character $\chi^{\mathrm{tot}}_{\mathrm{nspin}}[P]$ since they must multiply together to give a component with a character −1 here. This means that we have

$$\chi^{\mathrm{sw}}_{\mathrm{rve}}[P]^{+} = \prod(2I_a + 1)(-1)^{(2I_a)(n_a-1)}, \tag{8-27}$$

where the product contains one factor [as in Eq. (8-11)] for each set of n_a nuclei having spin I_a that are permuted by P (including sets of one nucleus for which $n_a=1$). The exponent $(2I_a)(n_a - 1)$ has been cleverly chosen since $2I_a$ will be odd for fermions and a permutation of n_a nuclei will be odd if $(n_a - 1)$ is odd. The product of two odd numbers is an odd number; the product of two even numbers, or of an odd and even number, is an even number. Thus only for an odd permutation of fermions will the product $(2I_a)(n_a - 1)$ be odd, and the character have the required opposite sign from the character in the representation $\Gamma^{\mathrm{tot}}_{\mathrm{nspin}}$.

In summary, from Eqs. (8-24) and (8-27), the characters in the representation $\Gamma^{\mathrm{sw}}_{\mathrm{rve}}$ of the MS group that gives the allowed rovibronic states and their nuclear spin statistical weights are given by

$$\chi^{\mathrm{sw}}_{\mathrm{rve}}[P] = 2\prod(2I_a + 1)(-1)^{(2I_a)(n_a-1)}, \tag{8-28}$$

for any nuclear permutation operation P in the MS group,[4] where the product contains one factor for each set of n_a nuclei having spin I_a permuted by P (including sets of one nucleus for which $n_a=1$). The characters in $\Gamma^{\mathrm{sw}}_{\mathrm{rve}}$ are zero for all the permutation-inversion operations in the MS group.

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[4] If the MS group contains no permutation-inversion elements (in which case the molecule will be optically active), then we still use Eq. (8-28) and the factor of two allows for the double parity degeneracy of Φ_{int}.

As an example we will apply Eq. (8-28) to the determination of the nuclear spin statistical weights for $^{14}NH_3$ molecule in the MS group $D_{3h}(M)$; we treat the effect of the elements $O = E$, (123), and (12) in detail.
For the operation E we have to divide the nuclei into four sets:
a=1. E leaves the proton numbered 1 alone so that $n_1 = 1$ and $I_1 = 1/2$.
a=2. E leaves the proton numbered 2 alone so that $n_2 = 1$ and $I_2 = 1/2$.
a=3. E leaves the proton numbered 3 alone so that $n_3 = 1$ and $I_3 = 1/2$.
a=4. E leaves the nitrogen alone so that $n_4 = 1$ and $I_4 = 1$.
Thus

$$\begin{aligned}\chi^{sw}_{rve}[E] &= 2 \times \{[2 \times (1/2) + 1](-1)^{(2\times 1/2)(1-1)} \\ &\quad \times [2 \times (1/2) + 1](-1)^{(2\times 1/2)(1-1)} \\ &\quad \times [2 \times (1/2) + 1](-1)^{(2\times 1/2)(1-1)} \\ &\quad \times (2 \times 1 + 1)(-1)^{(2\times 1)(1-1)}\} \\ &= +48. \end{aligned} \tag{8-29}$$

For the operation (123) we have to divide the nuclei into two sets:
a=1. (123) cyclically permutes the three protons so that $n_1 = 3$ and $I_1 = 1/2$.
a=2. (123) leaves the nitrogen alone so that $n_2 = 1$ and $I_2 = 1$.
Thus

$$\begin{aligned}\chi^{sw}_{rve}[(123)] &= 2 \times \{[2 \times (1/2) + 1](-1)^{(2\times 1/2)(3-1)} \\ &\quad \times (2 \times 1 + 1)(-1)^{(2\times 1)(1-1)}\} \\ &= +12. \end{aligned} \tag{8-30}$$

For the operation (12) we have to divide the nuclei into three sets:
a=1. (12) leaves nucleus numbered 3 alone so that $n_1 = 1$ and $I_1 = 1/2$.
a=2. (12) permutes nuclei numbered 1 and 2 so that $n_2 = 2$ and $I_2 = 1/2$.
a=3. (12) leaves the ^{14}N nucleus alone so that $n_3 = 1$ and $I_3 = 1$.
Thus

$$\begin{aligned}\chi^{sw}_{rve}[(12)] &= 2 \times \{[2 \times (1/2) + 1](-1)^{(2\times 1/2)(1-1)} \\ &\quad \times [2 \times (1/2) + 1](-1)^{(2\times 1/2)(2-1)} \\ &\quad \times (2 \times 1 + 1)(-1)^{(2\times 1)(1-1)}\} \\ &= -24. \end{aligned} \tag{8-31}$$

Combining the results of Eqs. (8-29)-(8-31) with the fact that the character of each permutation-inversion is zero leads directly to the allowed rovibronic species given in Eq. (8-21). The permutation (123) is even and the permutation (12) is an odd fermion permutation. By studying the results above one can see how the exponent $(2I_a)(n_a - 1)$ works. The results in Table B-4 of Appendix *B* can be used by the reader to test the application of Eq. (8-28).

Problem 8-3. The spherical top molecules $^{12}CH_4$ [with the protons labeled $H_1H_2H_3H_4$] and $^{192}Os^{16}O_4$ [with the oxygen nuclei labeled $O_1O_2O_3O_4$] both have the MS group $\boldsymbol{T}_d(M)$ whose character table is given in Table A-14. Determine the representation Γ_{rve}^{sw} for these two molecules (^{12}C, ^{192}Os, and ^{16}O nuclei all have $I = 0$).

Answer. From Table A-14 we see that we must determine the character of Γ_{rve}^{sw} under the three permutations E, (123), and (14)(23).

When we apply Eq. (8-28) to determine $\chi_{rve}^{sw}[E]$ for $^{12}CH_4$, each nucleus in the molecule forms a one-member set. The four one-member sets with $a = 1$, 2, 3, 4 each contains a proton so that $I_1 = I_2 = I_3 = I_4 = 1/2$, and the set with $a = 5$ contains the ^{12}C nucleus so that $I_5 = 0$. We calculate $\chi_{rve}^{sw}[E] = 32$ from Eq. (8-28). For (123), three protons labeled 1, 2, and 3 form a three-member set with $I_1 = 1/2$, proton 4 forms a one-member set with $I_2 = 1/2$, and the ^{12}C nucleus forms a one-member set with $I_3 = 0$. Thus $\chi_{rve}^{sw}[(123)] = 8$. Under (14)(23), the two proton pairs (1,4) and (2,3), respectively, each form a two-member set with $I_1 = I_2 = 1/2$, and the ^{12}C nucleus forms a one-member set with $I_3 = 0$, and we obtain $\chi_{rve}^{sw}[(14)(23)] = 8$. The remaining operations in $\boldsymbol{T}_d(M)$ are P^* operations, and for them $\chi_{rve}^{sw}[P^*] = 0$.

From the calculated characters we determine the reduction of Γ_{rve}^{sw} in terms of the irreducible representations of $\boldsymbol{T}_d(M)$ as

$$\Gamma_{rve}^{sw} = 5A_1 \oplus 5A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2, \tag{8-32}$$

where the coefficients are the nuclear spin statistical weights of $^{12}CH_4$.

For $^{192}Os^{16}O_4$, the derivation is analogous to that for $^{12}CH_4$ above. The only difference in applying Eq. (8-28) is that instead of four protons with $I = 1/2$ we now have four ^{16}O nuclei with $I = 0$. We derive $\chi_{rve}^{sw}[E] = \chi_{rve}^{sw}[(123)] = \chi_{rve}^{sw}[(14)(23)] = 2$ and thus

$$\Gamma_{rve}^{sw} = A_1 \oplus A_2. \tag{8-33}$$

In $Os^{16}O_4$, levels with rovibronic symmetry E, F_1, or F_2 in $\boldsymbol{T}_d(M)$ are missing.

Problem 8-4. The MS group $\boldsymbol{O}_h(M)$ of the octahedral molecule SF_6 (with the F nuclei labeled 1, 2, ... , 6) is given in Table A-15. Determine the representation Γ_{rve}^{sw} for $^{32}SF_6$ [^{32}S nuclei have $I = 0$, ^{19}F nuclei have $I = 1/2$].

Answer. Table A-15 shows that we must determine the character of Γ_{rve}^{sw} from Eq. (8-28) for the five permutation operations E, (145)(236), (13)(26(45), (1234), and (13)(24). Under all of these operations, the ^{32}S nucleus forms a one member set with $I = 0$. This set always contributes a factor of 1 to the character of Γ_{rve}^{sw}.

- Under the operation E the ^{19}F nuclei form six 1-member sets and $\chi_{rve}^{sw} = 128$.
- Under (145)(236), the ^{19}F nuclei form two 3-member sets and $\chi_{rve}^{sw} = 8$.

- Under (13)(26)(45), the ^{19}F nuclei form three 2-member sets and $\chi^{\text{sw}}_{\text{rve}} = -16$.
- Under (1234) the ^{19}F nuclei form a 4-member set and two 1-member sets, so $\chi^{\text{sw}}_{\text{rve}} = -16$.
- Under (13)(24) the ^{19}F nuclei form two 2-member sets and two 1-member sets, so $\chi^{\text{sw}}_{\text{rve}} = 32$.

The remaining operations in $\boldsymbol{O}_{\text{h}}(\text{M})$ are P^* operations, and for them $\chi^{\text{sw}}_{\text{rve}}[P^*] = 0$.

From the calculated characters we determine the reduction of $\Gamma^{\text{sw}}_{\text{rve}}$ in terms of the irreducible representations of $\boldsymbol{O}_{\text{h}}(\text{M})$ as

$$\begin{aligned}\Gamma^{\text{sw}}_{\text{rve}} &= 2A_{1\text{g}} \oplus 2A_{1\text{u}} \oplus 10A_{2\text{g}} \oplus 10A_{2\text{u}} \oplus 8E_{\text{g}} \\ &\oplus 8E_{\text{u}} \oplus 6F_{1\text{g}} \oplus 6F_{1\text{u}} \oplus 6F_{2\text{g}} \oplus 6F_{2\text{u}},\end{aligned} \tag{8-34}$$

where the coefficients are the spin statistical weights of ^{32}SF$_6$.

8.4.2 An example: NCCN

For the linear molecule NCCN (numbering the nuclei $N_1C_3C_4N_2$) symmetrical isotopomers have the MS group $\{E, (12)(34), E^*, (12)(34)^*\}$, called $\boldsymbol{D}_{\infty\text{h}}(\text{M})$, just as for acetylene [see Eq. (3-15)]. The character table is given in Table A-18 [where the operation (12) should be replaced by (12)(34)], and we label the irreducible representations $\Sigma_g{}^+$, $\Sigma_u{}^-$, $\Sigma_g{}^-$, and $\Sigma_u{}^+$. Unsymmetrical isotopomers of NCCN have the MS group $\boldsymbol{C}_{\infty\text{v}}(\text{M}) = \{E, E^*\}$ with the irreducible representations Σ^+ and Σ^- [see Table A-17].

We use Eq. (8-28) to derive the spin statistical weights for the four isotopomers ^{14}N^{12}C^{12}C^{14}N, ^{15}N^{12}C^{12}C^{15}N, ^{14}N^{13}C^{13}C^{14}N, and ^{15}N^{12}C^{12}C^{14}N. Letting I_α denote the spin of nucleus α (= 1, 2, 3, 4), then for all four isotopomers Eq. (8-28) gives

$$\chi^{\text{sw}}_{\text{rve}}[E] = 2(2I_1+1)(2I_2+1)(2I_3+1)(2I_4+1). \tag{8-35}$$

The first three isotopomers are symmetrical and the operation (12)(34) is a symmetry operation. When we apply Eq. (8-28) to determine $\chi^{\text{sw}}_{\text{rve}}[(12)(34)]$ for these molecules the nitrogen nuclei form one two-member set with spin $I_{\text{N}} = I_1 = I_2$, and the carbon nuclei form another two-member set with spin $I_{\text{C}} = I_3 = I_4$. Consequently

$$\chi^{\text{sw}}_{\text{rve}}[(12)(34)] = 2(2I_{\text{N}}+1)(2I_{\text{C}}+1)(-1)^{2(I_{\text{N}}+I_{\text{C}})}. \tag{8-36}$$

The remaining operations in the respective MS groups are P^* operations, and for them $\chi^{\text{sw}}_{\text{rve}}[P^*] = 0$.

It is straightforward to apply Eqs. (8-35) and (8-36) to the four isotopomers listed above (^{14}N nuclei have $I = 1$, ^{15}N and ^{13}C nuclei have $I = 1/2$, and ^{12}C nuclei have $I = 0$), and the results are summarized in Table 8-7. The table also gives the reduction of $\Gamma^{\text{sw}}_{\text{rve}}$ in terms of the irreducible representations of the MS group and thus the spin statistical weights for the four molecules.

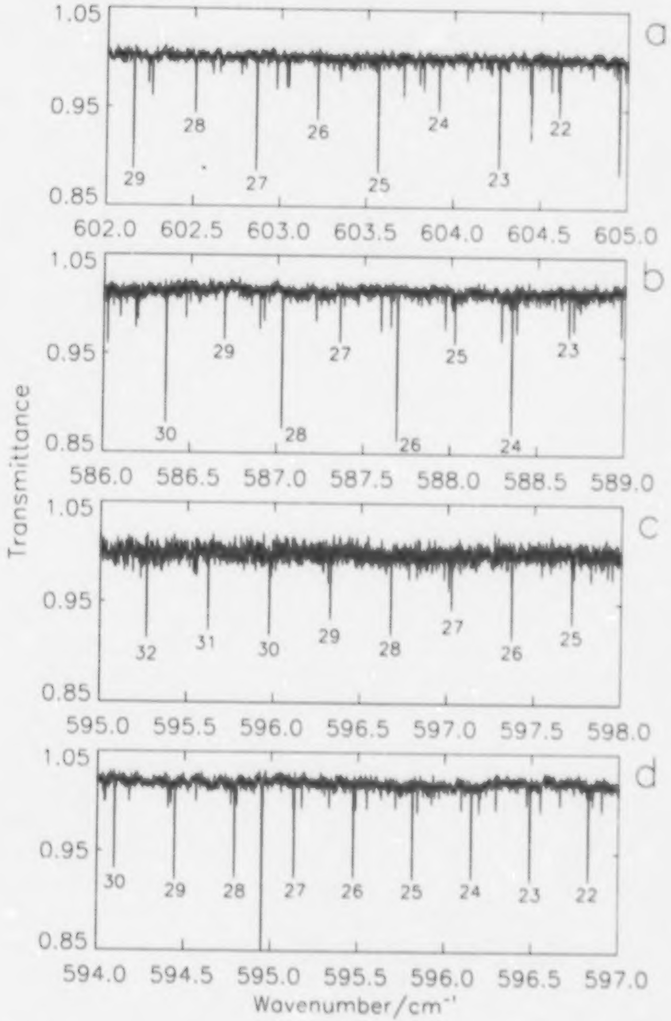

Fig. 8-1. Sections of the P-branch region of the $\nu_2^{0e} \leftarrow \nu_5^{1e}$ vibrational transition in the isotopomers a: $^{14}N^{12}C^{12}C^{14}N$, b: $^{15}N^{12}C^{12}C^{15}N$, c: $^{14}N^{13}C^{13}C^{14}N$, and d: $^{15}N^{12}C^{12}C^{14}N$ [Grecu, Winnewisser, and Winnewisser (1998)]. The lines are marked by their J'' values, and the intensity alternation resulting from the spin statistical weights is easily recognized. The intensity ratio $I[J''(\text{even})]/I[J''(\text{odd})]$ is 3/6 for $^{14}N^{12}C^{12}C^{14}N$, 3/1 for $^{15}N^{12}C^{12}C^{15}N$, 21/15 for $^{14}N^{13}C^{13}C^{14}N$, and 6/6 for $^{15}N^{12}C^{12}C^{14}N$ (see Appendix 8-1 for details).

Table 8-7

The representation $\Gamma_{\mathrm{rve}}^{\mathrm{sw}}$ and the statistical weights for rovibronic states of NCCN isotopomers

	E	$(12)(34)$	E^*	$(12)(34)^*$	$\Gamma_{\mathrm{rve}}^{\mathrm{sw}}$
$^{14}N^{12}C^{12}C^{14}N$:	18	6	0	0	$6\Sigma_g^+ \oplus 3\Sigma_g^- \oplus 6\Sigma_u^- \oplus 3\Sigma_u^+$
$^{15}N^{12}C^{12}C^{15}N$:	8	-4	0	0	$\Sigma_g^+ \oplus 3\Sigma_g^- \oplus \Sigma_u^- \oplus 3\Sigma_u^+$
$^{14}N^{13}C^{13}C^{14}N$:	72	-12	0	0	$15\Sigma_g^+ \oplus 21\Sigma_g^- \oplus 15\Sigma_u^- \oplus 21\Sigma_u^+$
$^{15}N^{12}C^{12}C^{14}N$:	12	-	0	-	$6\Sigma^+ \oplus 6\Sigma^-$

The $\Gamma_{\mathrm{rve}}^{\mathrm{sw}}$ in Table 8-7 indicate that for these four isotopomers there will be intensity alternations in their spectra that have ratios of 6/3, 1/3, 15/21 and 6/6, respectively (the last named, $^{15}N^{12}C^{12}C^{14}N$, having therefore no intensity alternation). Fig. 8-1 shows spectra of the four isotopomers exhibiting these intensity alternations. In Appendix 8-1 the details of the notation used, and the assignments made on the spectra, are given; they require rather extensive knowledge of material that is discussed in later chapters.

8.4.3 Another example: $^{13}C_{60}$

It is trivial to derive the spin statistical weights for the charismatic molecule $^{12}C_{60}$ [Kroto, Heath, O'Brien, Curl, and Smalley (1985)]. All 60 nuclei have zero spin, and so the molecule has one possible nuclear spin function of A_g symmetry in the molecular symmetry group $\boldsymbol{I}_h(M)$. The character table of the icosahedral group $\boldsymbol{I}_h(M)$ is given in Table A-16. The Pauli exclusion principle requires that the internal wavefunction of $^{12}C_{60}$ be invariant under any permutation of ^{12}C nuclei. That is, the internal wavefunction has A_g or A_u symmetry in $\boldsymbol{I}_h(M)$. Levels of $^{12}C_{60}$ with $\Gamma_{\mathrm{rve}} = A_g$ or A_u have a spin statistical weight of 1, and all other levels are missing.

For the isotopomer $^{13}C_{60}$ there are 2^{60} possible nuclear spin functions [^{13}C has $I = 1/2$], and the calculation of the spin statistical weights can be made to appear a formidable problem. We will determine them here using the method described in Section 8.4.1. That is, we will determine the representation $\Gamma_{\mathrm{rve}}^{\mathrm{sw}}$ of $\boldsymbol{I}_h(M)$ for the molecule $^{13}C_{60}$, and this is rather simple to do.

It would take up a lot of space to display the elements of $\boldsymbol{I}_h(M)$; each of them involves the 60 indices labeling the nuclei. The reader can use Fig. 8-2 together with Table A-16 to construct the MS group partners of the operations in the point group $\boldsymbol{I}_h$. One of the simpler MS group operations is $\hat{O}_i$, the partner of

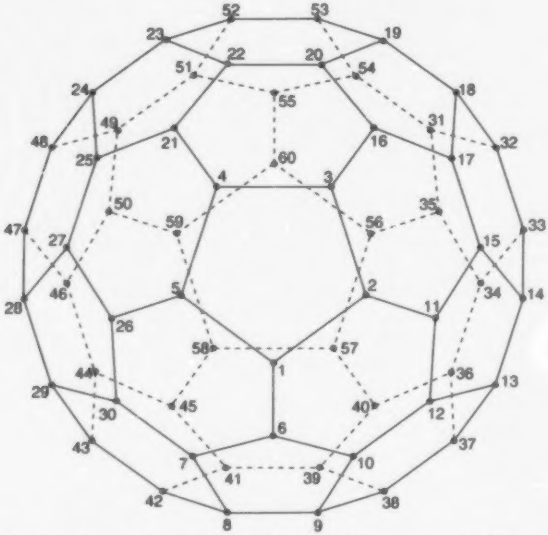

Fig. 8-2. The labeling of the nuclei used for the $^{13}C_{60}$ molecule. The nuclei 1-30 are in or above the plane of the paper; nuclei 31-60 are in or below this plane.

the point group inversion operation i [see Eq. (4-7)]. It is given by

$$\hat{O}_i = (1\ 60)(2\ 59)(3\ 58)(4\ 57)\ldots(29\ 32)(30\ 31)^*, \tag{8-37}$$

when the nuclei are labeled as in Fig. 8-2. That is, $\hat{O}_i$ is the product of 30 transpositions and the inversion E^*. The group $\boldsymbol{I}_h(M)$ is the direct product [see Section 5.7] of its permutation subgroup $\boldsymbol{I}(M)$ and the group $\{E, \hat{O}_i\}$:

$$\boldsymbol{I}_h(M) = \boldsymbol{I}(M) \otimes \{E, \hat{O}_i\}. \tag{8-38}$$

Therefore the class structure of $\boldsymbol{I}_h(M)$ is straightforwardly obtained from that of $\boldsymbol{I}(M)$. Each class in $\boldsymbol{I}(M)$ gives rise to two classes in $\boldsymbol{I}_h(M)$, one that contains the same elements as the $\boldsymbol{I}(M)$ class, and one that contains the elements obtained by combining each element in the $\boldsymbol{I}(M)$ class with $\hat{O}_i$ [see Section 5.8.2].

The classes $\mathcal{C}_k$ of $\boldsymbol{I}_h(M)$ are defined in the footnote of Table A-16. We apply Eq. (8-28) to the classes containing permutation operations:

- Under the operation E the nuclei form 60 1-member sets and $\chi^{\mathrm{sw}}_{\mathrm{rve}}[E] = 2 \times 2^{60}$.

- The elements in the classes $\mathcal{C}_2$ and $\mathcal{C}_3$ are all products of 12 five-cycles $(abcde)$. Thus, the nuclei form 12 five-member sets and Eq. (8-28) yields 2×2^{12} for the characters of $\Gamma^{\mathrm{sw}}_{\mathrm{rve}}$.

- The elements in the class $\mathcal{C}_4$ are products of 20 three-cycles (abc), so the nuclei form 20 three-member sets and the character $\chi^{\mathrm{sw}}_{\mathrm{rve}} = 2 \times 2^{20}$ for this class.

- The elements in the class $\mathcal{C}_5$ are products of 30 transpositions (ab), so the nuclei form 30 two-member sets and $\chi^{\mathrm{sw}}_{\mathrm{rve}} = 2 \times 2^{30}$.

The operations in the remaining classes of $\boldsymbol{I}_{\mathrm{h}}(\mathrm{M})$ are P^* operations, and for them $\chi^{\mathrm{sw}}_{\mathrm{rve}}[P^*] = 0$. The nonvanishing characters of $\Gamma^{\mathrm{sw}}_{\mathrm{rve}}$ are thus

$$\begin{array}{ccccc} E & \mathcal{C}_2 & \mathcal{C}_3 & \mathcal{C}_4 & \mathcal{C}_5 \\ 2^{61} & 2^{13} & 2^{13} & 2^{21} & 2^{31}. \end{array} \tag{8-39}$$

We have used the program system MAPLE [see, for example, Monagan, Geddes, Labahn, and Vorkoetter (1996)] to calculate the spin statistical weights as the coefficients $C^{(\Gamma_i)}$ in the reduction of $\Gamma^{\mathrm{sw}}_{\mathrm{rve}}$ in terms of the irreducible representation of $\boldsymbol{I}_{\mathrm{h}}(\mathrm{M})$,

$$\Gamma^{\mathrm{sw}}_{\mathrm{rve}} = \sum_{\Gamma_i} C^{(\Gamma_i)} \Gamma_i, \tag{8-40}$$

from Eq. (5-45) as exact, 17-digit integer values. The resulting weights are given in Table 8-8. These spin statistical weights were first obtained by Balasubramanian (1991) using an alternative method [see the Bibliographical Notes].

Table 8-8

The statistical weights of the rovibronic states of $^{13}C_{60}$

Γ_{rve}	Statistical weight
A_g/A_u	19 215 358 678 900 736
F_{1g}/F_{1u}	57 646 074 961 907 712
F_{2g}/F_{2u}	57 646 074 961 907 712
G_g/G_u	76 861 433 640 804 352
H_g/H_u	96 076 792 318 656 512

However, in any practical use of the statistical weights concerning intensity alternations in a spectrum it is inconceivable that results as precise as given in Table 8-8 will be needed, and a moment's thought shows a simple way to obtain statistical weights that are precise enough by inspection. From Eq. (8-39) we see that the characters under $\mathcal{C}_2$, $\mathcal{C}_3$, $\mathcal{C}_4$, and $\mathcal{C}_5$ are negligibly small in comparison to the character under E, and so we obtain from Eq. (5-45) the simple result that

$$C^{(\Gamma_i)} \approx \frac{1}{120}\, \chi^{\Gamma_i}[E]\, \chi^{\mathrm{sw}}_{\mathrm{rve}}[E], \tag{8-41}$$

where $\chi^{\mathrm{sw}}_{\mathrm{rve}}[E] = 2^{61}$ here, so that the statistical weights are in the approximate ratio of the dimensions $\chi^{\Gamma_i}[E]$ of the irreducible representations, which is 1:3:3:4:5. This is good to better than 1 part in 10^7.

Balasubramanian (1991) has obtained the spin statistical weights of $^{12}C_{60}H_{60}$ (which has the same weights as $^{13}C_{60}$) and $^{12}C_{60}D_{60}$. We extend these studies by considering $^{13}C_{60}H_{60}$ and $^{13}C_{60}D_{60}$. For these molecules, the characters of $\Gamma^{\rm sw}_{\rm rve}$ under the permutation operations of $\boldsymbol{I}_{\rm h}(\mathrm{M})$ are

$$\begin{array}{rccccc} & E & \mathcal{C}_2 & \mathcal{C}_3 & \mathcal{C}_4 & \mathcal{C}_5 \\ ^{13}\mathrm{C}_{60}\mathrm{H}_{60}: & 2^{121} & 2^{25} & 2^{25} & 2^{41} & 2^{61} \\ ^{13}\mathrm{C}_{60}\mathrm{D}_{60}: & 2^{61}3^{60} & 2^{13}3^{12} & 2^{13}3^{12} & 2^{21}3^{20} & 2^{31}3^{30}. \end{array} \qquad (8\text{-}42)$$

Reduction of the representations (using the program system MAPLE) produces the spin statistical weights given in Tables 8-9 and 8-10, respectively. In both cases [applying Eq. (8-41)] we obtain the very-close-to-exact statistical weight ratios of 1:3:3:4:5 by inspection.

Table 8-9

The statistical weights of the rovibronic states of $^{13}C_{60}H_{60}$

$\Gamma_{\rm rve}$	Statistical weight
A_g/A_u	22 153 799 929 748 598 169 960 860 333 637 632
F_{1g}/F_{1u}	66 461 399 789 245 793 356 959 976 865 660 928
F_{2g}/F_{2u}	66 461 399 789 245 793 356 959 976 865 660 928
G_g/G_u	88 615 199 718 994 391 526 920 837 182 521 344
H_g/H_u	110 768 999 648 742 989 696 880 598 004 531 200

Table 8-10

The statistical weights of the rovibronic states of $^{13}C_{60}D_{60}$

$\Gamma_{\rm rve}$	Statistical weight
A_g/A_u	814 561 299 678 154 291 488 767 806 377 392 301 451 223 040
F_{1g}/F_{1u}	2 443 683 899 034 462 874 466 082 345 208 800 010 378 924 032
F_{2g}/F_{2u}	2 443 683 899 034 462 874 466 082 345 208 800 010 378 924 032
G_g/G_u	3 258 245 198 712 617 165 954 850 151 586 192 309 653 364 736
H_g/H_u	4 072 806 498 390 771 457 443 617 957 959 928 452 664 524 800

8.5 CORRELATION TABLES WITH STATISTICAL WEIGHTS ADDED

Correlation tables and reverse correlation tables were introduced in Chapter 5, and we can add nuclear spin statistical weights to such tables. The tables then becomes useful in the identification of tunneling splitting patterns. The results in Tables 8-1 and 8-2 have been used to add statistical weights to the reverse correlation table $\boldsymbol{D}_{2\rm h}(\mathrm{M}) \rightarrow \boldsymbol{G}_{16}$ given in Table B-4(vi) in Appendix $\boldsymbol{B}$.

In Appendix ***B*** (Table B-4) reverse correlation tables with statistical weights are given for ammonia, methanol, methylsilane, acetone, hydrogen peroxide, ethylene, ethane, and methane [see also Watson (1965)].

Sometimes in complicated tunneling situations it is necessary to consider a reverse correlation table involving more than one group. The reverse correlation table for the groups $\boldsymbol{C}_2(\mathrm{M}) \rightarrow \boldsymbol{G}_4 \rightarrow \boldsymbol{G}_8$ for $\mathrm{H_2{}^{16}O_2}$, with statistical weights added, can be determined as an example. $\boldsymbol{C}_2(\mathrm{M})$ is the MS group if no tunneling splittings are resolved, $\boldsymbol{G}_4$ is the MS group if internal rotation tunneling splittings are resolved, and $\boldsymbol{G}_8$ is the CNPI group which allows for splittings due to the breaking and reforming of the OH bonds.

The allowed species of the complete internal wavefunction in the groups $\boldsymbol{C}_2(\mathrm{M})$, $\boldsymbol{G}_4$, and $\boldsymbol{G}_8$ are $2B$ (allowing for the parity double degeneracy), B_1 or B_2, and B_1'' or B_2'', respectively. The proton nuclear spin wavefunctions $|m_1, m_2\rangle = |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle, |-\frac{1}{2}, \frac{1}{2}\rangle$, and $|-\frac{1}{2}, -\frac{1}{2}\rangle$ generate the representations $3A \oplus B$, $3A_1 \oplus B_2$, and $3A_1' \oplus B_2''$ in the three groups, respectively. The reverse correlation of rovibronic levels of symmetry A and B in the $\boldsymbol{C}_2(\mathrm{M})$ group to the species of the $\boldsymbol{G}_4$ and $\boldsymbol{G}_8$ groups are determined to be as follows, and the statistical weights have been added.

$$A(2) \rightarrow \begin{cases} A_1(1) & \rightarrow A_1'(1) \oplus A_1''(0) \\ A_2(1) & \rightarrow A_2'(1) \oplus A_2''(0), \end{cases} \tag{8-43}$$

$$B(6) \rightarrow \begin{cases} B_1(3) & \rightarrow B_1'(0) \oplus B_1''(3) \\ B_2(3) & \rightarrow B_2'(0) \oplus B_2''(3). \end{cases} \tag{8-44}$$

We see that the final tunneling $\boldsymbol{G}_4 \rightarrow \boldsymbol{G}_8$ (if there were ever a possibility of resolving it) would not produce any splittings of the observed energy levels (although it would cause shifts in the levels), since in every case one of the pair of levels split by the tunneling has zero statistical weight and is missing.

We can add statistical weights to the reverse correlations given in Eqs. (5-86) and (5-87) for the water dimer and the result [using the $\Gamma(\mathrm{LH})$ notation for the irreducible representations of $\boldsymbol{G}_{16}$] is

$$A'(16) \rightarrow \begin{cases} B_1(12) & \rightarrow A_2{}^-(3) \oplus B_2{}^-(6) \oplus E^-(3) \\ A_1(4) & \rightarrow A_1{}^+(1) \oplus B_1{}^+(0) \oplus E^+(3), \end{cases} \tag{8-45}$$

$$A''(16) \rightarrow \begin{cases} B_2(12) & \rightarrow A_2{}^+(3) \oplus B_2{}^+(6) \oplus E^+(3) \\ A_2(4) & \rightarrow A_1{}^-(1) \oplus B_1{}^-(0) \oplus E^-(3). \end{cases} \tag{8-46}$$

The reverse correlations with statistical weights added for the benzene-water dimer using the chain of groups $\boldsymbol{C}_\mathrm{s}(\mathrm{M}) \rightarrow \boldsymbol{C}_{6\mathrm{v}}(\mathrm{M}) \rightarrow \boldsymbol{G}_{24} \rightarrow \boldsymbol{G}_{24} \otimes \mathcal{E}$ [see Eqs. (3-24)-(3-26) and Tables A-7 and A-27] is obtained as

$$A'(256) \rightarrow \begin{cases} A_1(40) & \rightarrow \begin{cases} A_{1s}(10) & \rightarrow A_{1s}{}^+(7) \oplus A_{1s}{}^-(3) \\ A_{1a}(30) & \rightarrow A_{1a}{}^+(21) \oplus A_{1a}{}^-(9), \end{cases} \\ B_2(56) & \rightarrow \begin{cases} B_{2s}(14) & \rightarrow B_{2s}{}^+(1) \oplus B_{2s}{}^-(13) \\ B_{2a}(42) & \rightarrow B_{2a}{}^+(3) \oplus B_{2a}{}^-(39), \end{cases} \\ E_1(88) & \rightarrow \begin{cases} E_{1s}(22) & \rightarrow E_{1s}{}^+(11) \oplus E_{1s}{}^-(11) \\ E_{1a}(66) & \rightarrow E_{1a}{}^+(33) \oplus E_{1a}{}^-(33), \end{cases} \\ E_2(72) & \rightarrow \begin{cases} E_{2s}(18) & \rightarrow E_{2s}{}^+(9) \oplus E_{2s}{}^-(9) \\ E_{2a}(54) & \rightarrow E_{2a}{}^+(27) \oplus E_{2a}{}^-(27), \end{cases} \end{cases} \tag{8-47}$$

and

$$A''(256) \rightarrow \begin{cases} A_2(40) & \rightarrow \begin{cases} A_{2s}(10) & \rightarrow A_{2s}{}^+(3) \oplus A_{2s}{}^-(7) \\ A_{2a}(30) & \rightarrow A_{2a}{}^+(9) \oplus A_{2a}{}^-(21), \end{cases} \\ B_1(56) & \rightarrow \begin{cases} B_{1s}(14) & \rightarrow B_{1s}{}^+(13) \oplus B_{1s}{}^-(1) \\ B_{1a}(42) & \rightarrow B_{1a}{}^+(39) \oplus B_{1a}{}^-(3), \end{cases} \\ E_1(88) & \rightarrow \begin{cases} E_{1s}(22) & \rightarrow E_{1s}{}^+(11) \oplus E_{1s}{}^-(11) \\ E_{1a}(66) & \rightarrow E_{1a}{}^+(33) \oplus E_{1a}{}^-(33), \end{cases} \\ E_2(72) & \rightarrow \begin{cases} E_{2s}(18) & \rightarrow E_{2s}{}^+(9) \oplus E_{2s}{}^-(9) \\ E_{2a}(54) & \rightarrow E_{2a}{}^+(27) \oplus E_{2a}{}^-(27). \end{cases} \end{cases} \tag{8-48}$$

APPENDIX 8-1: THE NCCN SPECTRA

We explain how the values of the statistical weights obtained for the different isotopomers of NCCN manifest themselves in the four experimental spectra shown in Fig. 8-1 [Grecu, Winnewisser, and Winnewisser (1998)]. Each spectrum is part of the P branch of the $\nu_2^{0e} \leftarrow \nu_5^{1e}$ vibrational transition. The labels ν_2 and ν_5 identify vibrational states of NCCN, and the superscripts give the value of the l quantum number [see Eq. (17-72)] together with the e/f label defined in Section 17.5.1. Each vibrational state ν_2^{0e} and ν_5^{1e} has a manifold of rotational energy levels, labeled by the rotational quantum number $J = l$, $l+1$, $l+2$, $l+3$, ... Each transition in the P branch of the vibrational transition $\nu_2^{0e} \leftarrow \nu_5^{1e}$ starts in a rotational level of the vibrational state ν_5^{1e} with the J-value J'' and ends in the ν_2^{0e} level with the J-value $J' = J'' - 1$. The complete P branch is the series of transitions with $J'' = 1, 2, 3, 4, 5, \ldots$. The lines in the series are roughly equidistantly spaced, and their wavenumber decreases with increasing J''.

For symmetrical isotopomers of NCCN with MS group $\boldsymbol{D}_{\infty\text{h}}(\text{M})$ the rovibrational symmetries are

$$\begin{array}{lll} & J\text{ even} & J\text{ odd} \\ \hline \nu_2^{0e} & \Sigma_g{}^+ & \Sigma_g{}^- \\ \nu_5^{1e} & \Sigma_u{}^+ & \Sigma_u{}^-. \end{array} \qquad (8\text{-}49)$$

For the unsymmetrical isotopomer of NCCN, with MS group $\boldsymbol{C}_{\infty v}(\mathrm{M})$, the rovibrational symmetries are obtained by omitting the 'g' and 'u' subscripts in Eq. (8-49). The symmetries in Eq. (8-49) can be deduced from Fig. 17-6; ν_2^{0e} is a vibronic state of $\Sigma_g{}^+$ symmetry in $\boldsymbol{D}_{\infty h}(\mathrm{EM})$ and ν_5^{1e} belongs to the ν_5^1 state of Π_u symmetry.

Equation (8-49) shows that transitions in the P branch of the $\nu_2^{0e} \leftarrow \nu_5^{1e}$ vibrational transition involve states of the MS group symmetries

$$\Sigma_g{}^- \leftarrow \Sigma_u{}^+ \text{ for } J'' \text{ even}, \qquad (8\text{-}50)$$

and

$$\Sigma_g{}^+ \leftarrow \Sigma_u{}^- \text{ for } J'' \text{ odd}. \qquad (8\text{-}51)$$

In order that an electric dipole transition can take place, the initial and final rovibronic states must be combined with the same nuclear spin state [see Chapter 14, in particular the discussion in connection with Eq. (14-29)]. For the P branch transitions considered here the statistical weight for the symmetrical isotopomers varies with the evenness or oddness of J''. For a given isotopomer of NCCN we denote the statistical weight for the states involved in transitions with even J'' by $g(\text{even})$, and for transitions with odd J'' by $g(\text{odd})$. The ratio $g(\text{even})/g(\text{odd})$ is 3/6 for $^{14}\mathrm{N}^{12}\mathrm{C}^{12}\mathrm{C}^{14}\mathrm{N}$, 3/1 for $^{15}\mathrm{N}^{12}\mathrm{C}^{12}\mathrm{C}^{15}\mathrm{N}$, 21/15 for $^{14}\mathrm{N}^{13}\mathrm{C}^{13}\mathrm{C}^{14}\mathrm{N}$, and 6/6 for $^{15}\mathrm{N}^{12}\mathrm{C}^{12}\mathrm{C}^{14}\mathrm{N}$ [see Table 8-7 together with Eq. (8-49)].

The ratio $g(\text{even})/g(\text{odd})$ determines, to a good approximation, the relative intensities of neighboring lines in the P branch of the $\nu_2^{0e} \leftarrow \nu_5^{1e}$ vibrational transition. The spectra in Fig. 8-1 give the transmittance as a function of wavenumber [see Eq. (14-2)]. At the wavenumber location of each allowed absorption line there is a dip in the transmittance, and the peak value of the dip is approximately proportional to the spin statistical weight. In Fig. 8-1 we have marked the individual lines in the P branch of the $\nu_2^{0e} \leftarrow \nu_5^{1e}$ vibrational transition by their J'' values, and it is seen that relative sizes of the transmittance dips are in good agreement with the $g(\text{even})/g(\text{odd})$ ratios.

The absolute intensities (i.e., the absolute values of the transmittance dips in Fig 8-1) are not proportional to the statistical weights. For example, the spectra of $^{15}\mathrm{N}^{12}\mathrm{C}^{12}\mathrm{C}^{14}\mathrm{N}$ and $^{15}\mathrm{N}^{13}\mathrm{C}^{13}\mathrm{C}^{14}\mathrm{N}$ have very similar absolute intensities regardless of the fact that $^{15}\mathrm{N}^{13}\mathrm{C}^{13}\mathrm{C}^{14}\mathrm{N}$ has four times as many nuclear spin states as $^{15}\mathrm{N}^{12}\mathrm{C}^{12}\mathrm{C}^{14}\mathrm{N}$. The reason is that the absolute intensity depends of the product of the spin statistical weight and the number of molecules populating each nuclear spin state. In $^{15}N^{13}C^{13}C^{14}N$ there are four times as many nuclear spin states than in $^{15}N^{12}C^{12}C^{14}N$, but each spin state in $^{15}N^{13}C^{13}C^{14}N$ has a population that is one fourth of the population of a state in $^{15}N^{12}C^{12}C^{14}N$. Consequently the product of spin statistical weight and population factor determining the intensity is the same for the two isotopomers. This is taken care of in the expression for the absolute intensity by dividing by the ***partition function*** [see Eqs. (14-3) and (14-4)].

BIBLIOGRAPHICAL NOTES

Missing levels

In Edition 1 (on page 310) it was conjectured that missing levels might appear if the nuclei in a molecule were sufficiently polarized by the electrons in the molecule to observably spoil I as a quantum number.

The problem has been reconsidered by Prof. G. W. F. Drake who explained to us that the interchange of nuclei remains an exact symmetry operation even if the nuclei are significantly polarized by the electrons in a molecule since identical nuclei will be identically polarized; also no amount of such polarization can turn a fermion into a boson or vice versa. In a private communication he further told us that what is needed is for there to be some way in which 'identical' nuclei become distinguishable in a molecule, and that Greenberg (1991) achieves this by introducing parastatistics, which is equivalent (at least in some formulations) to the postulate of hidden quantum numbers which would make the otherwise identical nuclei distinguishable. Prof. Drake explained to us that this is just like the considerations that lead to the idea that quarks have colour.

These ideas make it worthwhile to develop very sensitive methods for trying to see 'missing' spectral lines that involve so-called missing levels. For boson nuclei three negative results (at a spectral sensitivity of about 10^{-6}) for the $^{16}O_2$ molecule have been published [de Angelis, Gagliardi, Gianfrani, and Tino (1996), Hilborn and Yuca (1996), and Naus, de Lange and Ubachs (1997); see also Physics Today (1996)]. The infrared spectrum of the $C^{16}O_2$ molecule is a simple spectrum exhibiting missing lines, and it would be worthwhile to develop highly sensitive methods in order to try to see them (or at least to provide a very low upper limit on their existence). Missing lines that result from fermion nuclei in a molecule could also be looked for, and the spectrum of the NH_3 molecule would be a possible example. Stray fields and intermolecular interactions would presumably be of no consequence in making such missing spectral lines appear (unlike the situation for lines that appear due to parity non-conservation). The highest sensitivity achieved to date is[5] 5×10^{-13} by Ye, Ma and Hall (1998). In this paper the problems inherent in obtaining high sensitivity are carefully reviewed, and the possibility of using such high sensitivity methods to look for 'missing' levels is mentioned.

Spin statistical weights of icosahedral molecules

Balasubramanian (1981, 1985) has developed a algorithm for obtaining the total representation $\Gamma^{\mathrm{tot}}_{\mathrm{nspin}}$ generated by all possible nuclear spin functions of a molecule by means of so-called generalized character cycle indices. This method is applicable to very large, highly symmetrical molecules and Balasubramanian (1991) has used it to obtain the spin statistical weights for $^{13}C_{60}$, $^{12}C_{60}H_{60}$, and $^{12}C_{60}D_{60}$. If we are only interested in the spin statistical weights, the method described in Section 8.4.1, which involves the construction and reduction of the representation $\Gamma^{\mathrm{sw}}_{\mathrm{rve}}$, is probably easier to apply. For highly symmetric molecules it is easy to determine the characters of $\Gamma^{\mathrm{sw}}_{\mathrm{rve}}$ from Eq. (8-28), and the reduction of this representation gives the spin statistical weights directly. However, with Balasubramanian's method it is also possible to determine the symmetrized nuclear spin functions. One can also obtain them using the projection operator technique discussed in Section 6.3.

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[5] See Bibliographical Notes to Chapter 14 for a further discussion of this work.

Harter and Reimer (1992a) [see also the erratum Harter and Reimer (1992b) and the comment by Balasubramanian (1992)] have calculated the spin statistical weights for $^{13}C_{60}$ using a brute-force procedure that involves the generation of the irreducible representations in the CNP group $\boldsymbol{S}_{60}$ by means of Young tableau [see Section 9.4.5]. The correlation between $\boldsymbol{S}_{60}$ and its subgroup $\boldsymbol{I}$(M) [which Harter and Reimer call Y] is then used to obtain the symmetries of the nuclear spin functions in $\boldsymbol{I}$(M). The method for calculating spin statistical weights presented in Section 8.4.1 and the method of Balasubramanian (1981, 1985) are considerably easier to apply than the procedure of Harter and Reimer.

9

The Born-Oppenheimer Approximation and the Electronic Wavefunction

We return to the rovibronic Schrödinger equation given in Eq. (7-30), and explain how it is solved. We can break down the solution procedure into four stages which involve (a) setting it up in coordinates that facilitate the separation of variables in its solution, (b) making approximations so that there is some separation of variables, (c) solving the approximate and separable Schrödinger equation obtained, and (d) correcting for the approximations by using variational techniques or perturbation theory. In order that we can transform to the most suitable set of coordinates, we initially describe two general techniques for changing coordinates in a Schrödinger equation, and we apply one of them to the rovibronic Schrödinger equation. The most important approximation made for the purpose of solving the rovibronic Schrödinger equation is the Born-Oppenheimer approximation, and it allows the rovibronic Schrödinger equation to be solved in a two-step procedure. In the first step the electronic Schrödinger equation is solved with the nuclei held at fixed positions in space. In the second step the rotation-vibration Schrödinger equation is solved using the electronic energy from the first step in the nuclear potential energy function. At the end of the chapter we discuss the solution of the electronic Schrödinger equation, and we pay particular attention to the form of the electronic wavefunction.

9.1 THE ROVIBRONIC SCHRÖDINGER EQUATION

The rovibronic Hamiltonian H_{rve} is given in Eq. (7-29). When we insert this, using Eqs. (7-14), (7-15) and (7-19), into Eq. (7-30), we obtain the following expression for the rovibronic Schrödinger equation:

$$\left\{-\frac{\hbar^2}{2}\sum_{r=2}^{l}\frac{\nabla_r^2}{m_r}+\frac{\hbar^2}{2M}\sum_{r,s=2}^{l}\nabla_r\cdot\nabla_s+\sum_{r<s=1}^{l}\frac{C_rC_se^2}{4\pi\epsilon_0R_{rs}}-E_{\mathrm{rve}}\right\}$$
$$\times\Phi_{\mathrm{rve}}(X_2,\ldots,Z_l)=0, \qquad (9\text{-}1)$$

where there are l particles (nuclei and electrons) in the molecule, and E_{rve} and Φ_{rve} are the rovibronic eigenvalues and eigenfunctions, respectively. This is a $(3l-3)$ dimensional second order partial differential equation and for l greater than 2 (i.e., any molecule) this equation cannot be solved explicitly.

To solve the rovibronic Schrödinger equation given in Eq. (9-1) there are two methods which we will call the ***direct method*** and the ***indirect method***. The direct method is numerical and does not make use of any prior knowledge, understanding, or intuition that we have about molecules. In one possible direct numerical procedure that could, in principle, be used we divide each of the $(3l-3)$ coordinate directions $X_2, Y_2, Z_2, \ldots, Z_l$ into a grid of $(2n+1)$ equidistant points, where n is a very large integer. At these points the coordinate X_2 has the values

$$X_2^{(h)} = h\Delta, \quad h = -n, -n+1, -n+2, \ldots, n-1, n, \tag{9-2}$$

with similar equations for all the other coordinates $Y_2, Z_2, X_3, \ldots, Z_l$. In Eq. (9-2) Δ is a constant step length. We center a Gaussian function at each value $X_2^{(h)}$:

$$g_h(X_2) = \exp\left[-a\left(X_2 - X_2^{(h)}\right)^2\right], \tag{9-3}$$

where we are free to choose the (positive) value of the parameter a. The functions $g_{-n}(X_2)$, $g_{-n+1}(X_2)$, $\ldots$, $g_{n-1}(X_2)$, $g_n(X_2)$ constitute a sequence of $(2n+1)$ "Gaussian nipples" distributed along X_2 from $-n\Delta$ to $+n\Delta$. If we distribute similar functions along all the other coordinate directions Y_2, Z_2, $X_3, \ldots, Z_l$ we can model a real wavefunction as

$$\Phi_{\mathrm{rve}}(X_2, \ldots, Z_l) = \sum_a c_a \prod_{r=2}^{l} g_{h_{X_r}}(X_r) g_{h_{Y_r}}(Y_r) g_{h_{Z_r}}(Z_r), \tag{9-4}$$

where a is summed over all $(2n+1)(3l-3)$ sets of points at which the Gaussians are centered ($h_{X_2} = -n$ to $+n, \ldots, h_{Z_l} = -n$ to $+n$), and the c_a are expansion coefficients. For modeling a complex wavefunction we need two parameterized functions of this type, one for the real part and one for the imaginary part. Equation (9-4) involves numerical approximation, but if we make Δ very small and n very large, so that the Gaussian functions are very closely spaced and at the same time sample a large part of $X_2, Y_2, Z_2, \ldots, Z_l$ space, then this will model the wavefunction satisfactorily. We insert Eq. (9-4) into the Schrödinger equation Eq. (9-1), and solve to determine the rovibronic energies E_{rve} and the expansion coefficients c_a. We would use a slightly modified version of the matrix diagonalization technique described by Eqs. (6-145)-(6-162); the modification is made necessary by the fact that the basis functions $\prod_{r=2}^{l} g_{h_{X_r}}(X_r) g_{h_{Y_r}}(Y_r) g_{h_{Z_r}}(Z_r)$ are not normalized and orthogonal. This type of basis set has been used in actual calculations of molecular rotation-vibration energies and is known as a ***distributed Gaussian basis (DGB)***.

In a numerical procedure, such as that outlined above, we would solve the Schrödinger equation in a completely general way, but since the basis functions we use [the $\prod_{r=2}^{l} g_{h_{X_r}}(X_r) g_{h_{Y_r}}(Y_r) g_{h_{Z_r}}(Z_r)$ functions] are very different from the rovibronic eigenfunctions $\Phi_{\mathrm{rve}}(X_2, \ldots, Z_l)$ of the molecule, we will need a gigantic number of basis functions in the linear combinations of Eq. (9-4) to represent satisfactorily the eigenfunctions. Consequently, we would have to diagonalize an enormously large matrix and the procedure could only be carried out by means of an extremely powerful computer. To solve Eq. (9-1) numerically with a precision that is comparable to the best experiment is impossibly difficult (except for the very lowest eigenstates of three and four particle systems such as H_2^+ and H_2) and hence for practical reasons we use the indirect method. In the indirect method of solving Eq. (9-1) we also represent the rovibronic eigenfunctions Φ_{rve} as linear combinations of basis functions in a manner analogous to Eq. (9-4), but we aim at choosing the basis functions in such a way that they resemble the eigenfunctions as much as possible. We determine suitable basis functions by making approximations which simplify the Hamiltonian of the molecule. The Hamiltonian can be simplified to an extent where the Schrödinger equation associated with it can be solved fairly straightforwardly, analytically and/or numerically. Because of the approximations made, the resulting eigenfunctions, Φ^0_{rve} say, of the simplified Hamiltonian are not the true rovibronic wavefunctions Φ_{rve}, but we can express Φ_{rve} as a linear combination of Φ^0_{rve} functions and determine the expansion coefficients in these linear combinations, and the energies E_{rve} associated with the wavefunctions Φ_{rve}, by matrix diagonalization as described in Eqs. (6-145)-(6-162). In most cases, the approximations made in order to obtain the functions Φ^0_{rve} are such that the spectrum of the simplified molecule will reproduce correctly the gross features of the true spectrum. This means that the eigenfunctions Φ^0_{rve} of the simplified Hamiltonian are similar to the true wavefunctions Φ_{rve}. Consequently, when we obtain the wavefunctions Φ_{rve} and the corresponding energies by diagonalizing a matrix representation of the rovibronic Hamiltonian H_{rve} in a basis of Φ^0_{rve} functions, the matrix will be relatively small so that it will be easy to diagonalize it. If we diagonalize the matrix numerically we have solved the rovibronic Schrödinger equation in a *variational calculation*. However, because the basis functions used in setting up the matrix, Φ^0_{rve}, are similar to the eigenfunctions Φ_{rve}, it is possible that the matrix will be so close to being diagonal that we can diagonalize it analytically using *perturbation techniques*. In the indirect approach, we first make algebraic approximations and then correct for the approximations by matrix diagonalization.

Although solving the Schrödinger equation by the indirect method is forced on us as a practical necessity it has the desirable consequence of allowing us to understand the solutions. The reason for this is that in the course of making the approximations we introduce many concepts that give us a physical insight into the behavior of the nuclei and electrons in the molecule. Some of the more important concepts introduced are electronic state, molecular orbital, potential energy surface, equilibrium nuclear structure, and dipole moment function. We say we understand the solutions in that we can appreciate the pattern of the energy levels and form of the wavefunction for a given molecule without solving Eq. (9-1), and we appreciate in a general way how they will vary from one molecule to another.

Of the approximations that we make in solving Eq. (9-1) the main one is the Born-Oppenheimer approximation. As a result of this approximation we solve the rovibronic Schrödinger equation by first solving the electronic Schrödinger equation at many fixed nuclear geometries, and then solving the rotation-vibration Schrödinger equation for the nuclei. In solving the electronic Schrödinger equation the molecular orbital approximation is usually made; this leads to a separate Schrödinger equation for each electron and to electronic wavefunctions that are expressed in terms of one-electron molecular orbital functions. In solving the rotation-vibration Schrödinger equation we make the rigid rotor approximation, and we model the vibrational motion in some way, typically as a system of non-interacting harmonic oscillators, i.e., we make the ***harmonic oscillator approximation***. The approximate rotation-vibration Schrödinger equation obtained is separable, and the eigenfunctions are each the product of a rotational wavefunction in three variables and a vibrational wavefunction which, in the harmonic oscillator approximation, is the product of $(3N-6)$ harmonic oscillator wavefunctions, where there are N nuclei in the molecule [for a linear molecule the rotational wavefunction involves two coordinates and the vibrational one involves $(3N-5)$ coordinates; see Chapter 17]. These approximations are all made on the basis of the phenomenology of molecular behavior rather than on the basis of an abstract mathematical study of the partial differential equations involved.

We must be able to correct for the approximations made in the indirect method of solving Eq. (9-1) if we are to achieve a precise solution. We allow for anharmonicity, centrifugal distortion, and Coriolis coupling in the rotation-vibration problem (by using variational theory or perturbation theory) and for electron correlation in the electronic problem (usually by using variational theory). Finally corrections may have to be made to allow for the breakdown of the Born-Oppenheimer approximation. For our purposes of symmetry labeling molecular energy levels the form of the approximate wavefunctions will be very important since it is from these that we will obtain the symmetry labels.

Before making the above approximations it is necessary to find the most appropriate $(3l-3)$ coordinates for the Schrödinger equation. We change coordinates in order to facilitate the separation of variables in the equation that is obtained after making the approximations, and the choice of coordinates is nearly as important as the choice of approximation, especially for the rotation-vibration Schrödinger equation. We choose the coordinates with an eye to the approximations we plan to make. In the present chapter, we discuss general techniques for changing the coordinates in a Schrödinger equation, and we transform the rovibronic Schrödinger equation to a form suitable for making the Born-Oppenheimer approximation. The choice of the most appropriate coordinates in the rotation-vibration Schrödinger equation is the subject of Chapter 10.

9.2 TWO METHODS FOR CHANGING COORDINATES IN A SCHRÖDINGER EQUATION

Here we discuss two methods for changing coordinates in a Schrödinger equation, and we use the Schrödinger equation of the hydrogen atom as a convenient example. The coordinate change will be from Cartesian coordinates to polar coordinates:

(I) The first method for changing coordinates involves (a) setting up the classical Hamiltonian in Cartesian coordinates, (b) using the quantum mechanical postulates to derive the quantum mechanical Hamiltonian, and (c) changing coordinates in the resultant Schrödinger equation using the *chain rule*. This method was used in Chapter 7 when we changed from $(\mathrm{X}_1, \mathrm{Y}_1, \mathrm{Z}_1, \ldots, \mathrm{X}_l, \mathrm{Y}_l, \mathrm{Z}_l)$ to $(\mathrm{X}_0, \mathrm{Y}_0, \mathrm{Z}_0, X_2, Y_2, Z_2, \ldots, X_l, Y_l, Z_l)$ coordinates in order to achieve a separation of the translational part of the Hamiltonian [see Eqs. (7-2)-(7-18)].

(II) The second method for changing coordinates involves (a) setting up the classical Hamiltonian in Cartesian coordinates as before, (b) changing coordinates in the classical Hamiltonian expression, and (c) using the quantum mechanical postulates plus the ***Podolsky trick*** to change this to the quantum mechanical Hamiltonian in the new coordinates. This alternative procedure is traditionally used in the derivation of the rotation-vibration Hamiltonian of a polyatomic molecule [see Chapter 11 of Wilson, Decius, and Cross (1955)].

Both methods lead to the same wave equation but when many curvilinear coordinates are involved it is often much quicker to use Method II.

9.2.1 Method I. Using the chain rule

Using a space fixed (X, Y, Z) axis system for the proton (1) and electron (2) of a hydrogen atom, the classical energy is given by

$$E = \frac{m_1}{2}(\dot{\mathrm{X}}_1^2 + \dot{\mathrm{Y}}_1^2 + \dot{\mathrm{Z}}_1^2) + \frac{m_2}{2}(\dot{\mathrm{X}}_2^2 + \dot{\mathrm{Y}}_2^2 + \dot{\mathrm{Z}}_2^2) - \frac{e^2}{4\pi\epsilon_0[(\mathrm{X}_1 - \mathrm{X}_2)^2 + (\mathrm{Y}_1 - \mathrm{Y}_2)^2 + (\mathrm{Z}_1 - \mathrm{Z}_2)^2]^{1/2}}. \tag{9-5}$$

In order to use the quantum mechanical postulates for obtaining the quantum mechanical Hamiltonian operator we must put E into Hamiltonian form, i.e., express it in terms of coordinates and momenta, and this expression is

$$H = \frac{1}{2m_1}(P_{\mathrm{X}_1}^2 + P_{\mathrm{Y}_1}^2 + P_{\mathrm{Z}_1}^2) + \frac{1}{2m_2}(P_{\mathrm{X}_2}^2 + P_{\mathrm{Y}_2}^2 + P_{\mathrm{Z}_2}^2) - \frac{e^2}{4\pi\epsilon_0[(\mathrm{X}_1 - \mathrm{X}_2)^2 + (\mathrm{Y}_1 - \mathrm{Y}_2)^2 + (\mathrm{Z}_1 - \mathrm{Z}_2)^2]^{1/2}}, \tag{9-6}$$

where $P_{\mathrm{X}_1} = m_1\dot{\mathrm{X}}_1$, etc. Using the quantum mechanical postulates we replace

P_{X_1} by $-i\hbar\partial/\partial X_1$ etc. to obtain

$$H = -\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial X_1^2} + \frac{\partial^2}{\partial Y_1^2} + \frac{\partial^2}{\partial Z_1^2}\right) - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial X_2^2} + \frac{\partial^2}{\partial Y_2^2} + \frac{\partial^2}{\partial Z_2^2}\right)$$
$$- \frac{e^2}{4\pi\epsilon_0[(X_1 - X_2)^2 + (Y_1 - Y_2)^2 + (Z_1 - Z_2)^2]^{1/2}} \tag{9-7}$$

and the Schrödinger equation is

$$H\Phi_n(X_1, Y_1, Z_1, X_2, Y_2, Z_2) = E_n\Phi_n(X_1, Y_1, Z_1, X_2, Y_2, Z_2). \tag{9-8}$$

Having obtained the Schrödinger equation, Eq. (9-8), we change coordinates in it in a manner that allows a separation of the equation into explicitly soluble parts. The first coordinate change we make is from $(X_1, Y_1, Z_1, X_2, Y_2, Z_2)$ to (X_0, Y_0, Z_0, X, Y, Z), where the coordinates of the center of mass are (X_0, Y_0, Z_0) in the (X, Y, Z) axis system, and the coordinates of the electron are (X, Y, Z) in an (X, Y, Z) axis system parallel to the (X, Y, Z) axis system but with origin at (X_0, Y_0, Z_0). We make this coordinate change since we know that the potential function is independent of the location of the center of mass so that in these coordinates we are able to separate the translational motion [see Eq. (7-33)] leaving the Schrödinger equation for the internal motion [see Eq. (7-36)] as

$$\left[-\frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right) - \frac{e^2}{4\pi\epsilon_0(X^2 + Y^2 + Z^2)^{1/2}}\right]\Phi_{\text{int}}^{(n)}(X, Y, Z)$$
$$= E_{\text{int}}^{(n)}\Phi_{\text{int}}^{(n)}(X, Y, Z), \tag{9-9}$$

where $n = 1, 2, 3, \ldots$ labels the different solutions, and we are neglecting the difference between m_2, the mass of the electron, and the reduced mass $m_1m_2/(m_2 + m_1)$, where m_1 is the mass of the proton. Since the potential energy only depends on r, the separation of the proton and electron, we can separate the variables further by changing from Cartesian coordinates (X, Y, Z) to polar coordinates (r, θ, ϕ), where (θ, ϕ) are the polar angles in the (X, Y, Z) axis system of the vector pointing from the proton to the electron, i.e.,

$$X = r\sin\theta\cos\phi, \tag{9-10}$$

$$Y = r\sin\theta\cos\phi, \tag{9-11}$$

and

$$Z = r\cos\theta. \tag{9-12}$$

This coordinate change in a partial differential equation presents some problems since it is to a *curvilinear* coordinate system but this is well understood [see, for example, pages 172-178 in Margenau and Murphy (1956)]. The Schrödinger equation becomes

$$\left\{ -\frac{\hbar^2}{2m_2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\right\}\Phi_{\text{int}}^{(n)}(r,\theta,\phi) = E_{\text{int}}^{(n)}\Phi_{\text{int}}^{(n)}(r,\theta,\phi), \tag{9-13}$$

where the $\Phi_{\text{int}}^{(n)}$ are normalized with

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\Phi_{\text{int}}^{(n)*}\Phi_{\text{int}}^{(m)}r^2\sin\theta\,dr\,d\theta\,d\phi = \delta_{nm}. \tag{9-14}$$

The two important facts about such a coordinate change are the transformation properties of the differential operator [i.e., the identity of the terms within the square brackets from Eqs. (9-9) and (9-13)], and the volume element for the integration ($d\tau = dX\,dY\,dZ = r^2\sin\theta\,dr\,d\theta\,d\phi$). The chain rule [see Eqs. (7-8) and (7-9)] is used in determining the transformations that occur in the differential operators as a result of a coordinate change, and standard formulas are used to determine the volume element in the new coordinates [see, for example, Eq. (5-7) in Margenau and Murphy (1956)].

Equation (9-13) can be separated into a radial (r) part and an angular (θ,ϕ) part, and each of these separate Schrödinger equations can be solved explicitly. In the rovibronic Schrödinger equation of a molecule it is necessary to make some approximations, after making the coordinate changes, in order to separate the variables.

9.2.2 Method II. Using the Podolsky trick

The above technique for obtaining the wave equation in polar coordinates for a hydrogen atom involves changing coordinates in a partial differential equation. We now discuss the alternative procedure (II) in which we make all the coordinate changes in the classical Hamiltonian expression.

Changing coordinates from ($\mathrm{X}_1, \mathrm{Y}_1, \mathrm{Z}_1, \mathrm{X}_2, \mathrm{Y}_2, \mathrm{Z}_2$) to ($\mathrm{X}_0, \mathrm{Y}_0, \mathrm{Z}_0, X, Y, Z$) in the classical energy expression of Eq. (9-5) gives

$$E = \frac{m_1+m_2}{2}(\dot{\mathrm{X}}_0^2+\dot{\mathrm{Y}}_0^2+\dot{\mathrm{Z}}_0^2)+\frac{m_2}{2}(\dot{X}^2+\dot{Y}^2+\dot{Z}^2) - \frac{e^2}{4\pi\epsilon_0(X^2+Y^2+Z^2)^{1/2}}, \tag{9-15}$$

where we again neglect the difference between the mass of the electron and the reduced mass. After writing $\dot{\mathrm{X}}_0 = P_{\mathrm{X}_0}/(m_2+m_1)$ and replacing P_{X_0} by $\hat{P}_{\mathrm{X}_0} = -i\hbar\partial/\partial\mathrm{X}_0$, etc., the first term in Eq. (9-15) leads to the translational Hamiltonian operator; the remainder is the internal energy E_{int}. Changing to polar coordinates [see Eqs. (9-10)-(9-12)] we obtain

$$E_{\text{int}} = \frac{m_2}{2}(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2 \sin^2\theta) - \frac{e^2}{4\pi\epsilon_0 r}. \tag{9-16}$$

We must express this in Hamiltonian form, i.e., in terms of the coordinates and their *conjugate momenta*, before using the quantum mechanical postulates. The momentum p_i conjugate to the coordinate q_i, in a system having kinetic energy T and potential energy V, is defined by the equation,

$$p_i = \partial(T - V)/\partial\dot{q}_i. \tag{9-17}$$

If the system is such that V is independent of the velocities $\dot{q}_i$ then V can be omitted in this equation. In the hydrogen atom the conjugate momenta are

$$P_r = \frac{\partial T}{\partial \dot{r}} = m_2\dot{r}, \tag{9-18}$$

$$P_\theta = \frac{\partial T}{\partial \dot{\theta}} = m_2 r^2\dot{\theta}, \tag{9-19}$$

and

$$P_\phi = \frac{\partial T}{\partial \dot{\phi}} = m_2 r^2\dot{\phi}\sin^2\theta. \tag{9-20}$$

Replacing the velocities in Eq. (9-16) by the momenta, using Eqs. (9-18)-(9-20), we obtain the classical energy in Hamiltonian form as

$$H_{\text{int}} = \frac{P_r^2}{2m_2} + \frac{P_\theta^2}{2m_2 r^2} + \frac{P_\phi^2}{2m_2 r^2\sin^2\theta} - \frac{e^2}{4\pi\epsilon_0 r}. \tag{9-21}$$

To convert to the quantum mechanical Hamiltonian operator we might think that we could make the replacements

$$P_r \rightarrow \hat{P}_r = -i\hbar\frac{\partial}{\partial r}, \tag{9-22}$$

$$P_\theta \rightarrow \hat{P}_\theta = -i\hbar\frac{\partial}{\partial \theta}, \tag{9-23}$$

and

$$P_\phi \rightarrow \hat{P}_\phi = -i\hbar\frac{\partial}{\partial \phi}, \tag{9-24}$$

which would give

$$\hat{H}_{\text{int}} = -\frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2m_2 r^2}\frac{\partial^2}{\partial \theta^2} - \frac{\hbar^2}{2m_2 r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2} - \frac{e^2}{4\pi\epsilon_0 r}. \tag{9-25}$$

Equation (9-25) is not the same as the Hamiltonian operator in Eq. (9-13); in Eq. (9-13) r^2 occurs between the $\partial/\partial r$ factors and $\sin\theta$ occurs between the $\partial/\partial\theta$ factors. This method for changing coordinates has not led to the correct Schrödinger equation.

We see from the above that although the translational Hamiltonian operator is obtained correctly from the classical Hamiltonian expression by making the replacements $P_{X_0} = -i\hbar\partial/\partial X_0$, etc., the internal Hamiltonian operator is not obtained correctly from the classical expression in Eq. (9-21) by making the replacement of P_r by $-i\hbar\partial/\partial r$, etc. The reason for this is that to obtain the Hamiltonian operator from the classical Hamiltonian expression by using the quantum mechanical postulates we can only replace the momentum p_i by $-i\hbar\partial/\partial q_i$ (where p_i is conjugate to q_i) if q_i is a Cartesian coordinate. In our case r, θ, and ϕ are not Cartesian coordinates.

All is not lost, however, since Podolsky (1928) has shown that we can still set up the classical Hamiltonian in terms of general coordinates q_i and conjugate momenta p_i and replace the p_i by $-i\hbar\partial/\partial q_i$ to obtain the Hamiltonian operator, as long as we are careful about how we arrange the classical expression. Working backwards from the correct Hamiltonian operator in q_i and $-i\hbar\partial/\partial q_i$ we can see how it is necessary to arrange the way we write the classical Hamiltonian in terms of p_i and q_i so that replacement of p_i by $-i\hbar\partial/\partial q_i$ will yield the correct Hamiltonian operator. This recipe, or *Podolsky trick*, will now be explained [see also Smith (1934), Section 11-3 in Wilson, Decius, and Cross (1955), and the Appendix of Watson (1970)].

We can write the classical energy of a system of particles in general coordinates q and velocities $\dot{q}$ as

$$E = \frac{1}{2}\sum_{i,j} g_{ij}\dot{q}_i\dot{q}_j + V(q_i), \tag{9-26}$$

where the coefficients g_{ij} can be functions of the coordinates q_i. Expressing this in terms of momenta p_i conjugate to the coordinates [see Eq. (9-17)] we obtain the energy in Hamiltonian form as

$$H = \frac{1}{2}\sum_{i,j} g^{ij}p_ip_j + V(q_i), \tag{9-27}$$

where the matrix of g^{ij} is the inverse of the matrix of g_{ij}. At this stage we cannot say that the Hamiltonian operator is obtained from this by replacing p_i by $-i\hbar\partial/\partial q_i$, etc. unless all the coordinates are Cartesian. Podolsky (1928) showed that by rewriting H in the form

$$H = \frac{1}{2}g^{1/4}\sum_{i,j} p_i g^{-1/2}g^{ij}p_j g^{1/4} + V(q_i), \tag{9-28}$$

where g is the determinant of the matrix of g^{ij}, the Hamiltonian operator *is* correctly obtained by replacing p_i by $-i\hbar\partial/\partial q_i$, etc. Since the momenta and coordinates all commute in the classical expressions we see that Eqs. (9-27) and (9-28) are identical. However, in the derived Hamiltonian operator,

$$\hat{H} = \frac{1}{2}g^{1/4}\sum_{i,j}\left(-i\hbar\frac{\partial}{\partial q_i}\right)g^{-1/2}g^{ij}\left(-i\hbar\frac{\partial}{\partial q_j}\right)g^{1/4} + V(q_i), \tag{9-29}$$

the operators $\partial/\partial q_i$ and $\partial/\partial q_j$ will not commute with the coordinates, and so Eq. (9-29) is not the same as would be obtained by replacing p_i by $-i\hbar\partial/\partial q_i$, etc., in Eq. (9-27).

One final point concerns the volume element in the integration of the eigenfunctions of the Hamiltonian operator in Eq. (9-29). The volume element using $\hat{H}$ of Eq. (9-29) will be $dq_1\, dq_2 \cdots dq_n$, but we want to obtain eigenfunctions normalized with volume element $d\tau = dX_1\, dY_1\, dZ_1 \cdots$ in general. We write this volume element as $d\tau = s\,dq_1\, dq_2 \cdots dq_n$, where s is the *weight factor* involved in the coordinate transformation from Cartesian to general coordinates. To obtain eigenfunctions normalized with the appropriate volume element we must write the classical Hamiltonian in the form

$$H = \frac{1}{2}s^{-1/2}g^{1/4}\left[\sum_{i,j}p_i g^{-1/2}g^{ij}p_j\right]g^{1/4}s^{1/2} + V(q_i), \tag{9-30}$$

before making the replacements $p_i = -i\hbar\partial/\partial q_i$, etc., to give $\hat{H}$. The weight factor is easy to determine [see Eq. (5-7) in Margenau and Murphy (1956)], and for the coordinates used in the Hamiltonian for the hydrogen atom

$$s = r^2 \sin\theta. \tag{9-31}$$

Problem 9-1. Check that the Podolsky trick works by using it to obtain the Hamiltonian operator for the hydrogen atom from the classical expression of Eq. (9-21) and comparing the result with the Hamiltonian obtained in Eq. (9-13) by the Method I derivation.

Answer. To use the Podolsky trick it is necessary to determine g and to rewrite the Hamiltonian of Eq. (9-21) in the form of Eq. (9-30). From Eq. (9-21) we see that

$$g^{rr} = m_2^{-1}, \tag{9-32}$$

$$g^{\theta\theta} = m_2^{-1}r^{-2}, \tag{9-33}$$

and

$$g^{\phi\phi} = m_2^{-1}(r\sin\theta)^{-2}; \tag{9-34}$$

all other elements g^{ij} vanish. Using these results, and Eq. (9-31) for the weight factor s, we deduce that

$$g = m_2^{-3}r^{-4}(\sin\theta)^{-2}, \tag{9-35}$$

and that Eq. (9-21) written in the form of Eq. (9-30) is

$$\begin{aligned} H = {} & \frac{1}{2}[m_2^{-3/4} r^{-2} (\sin\theta)^{-1}]\{P_r [m_2^{3/2} r^2 \sin\theta] m_2^{-1} P_r \\ & + P_\theta [m_2^{3/2} r^2 \sin\theta] m_2^{-1} r^{-2} P_\theta \\ & + P_\phi [m_2^{3/2} r^2 \sin\theta] m_2^{-1} (r\sin\theta)^{-2} P_\phi\} m_2^{-3/4} - e^2/(4\pi\epsilon_0 r). \end{aligned} \qquad (9\text{-}36)$$

Since this is in the form prescribed by Podolsky we can obtain the Hamiltonian operator by making the replacements of Eqs. (9-22)-(9-24), which gives

$$\begin{aligned} H = {} & -\frac{\hbar^2}{2m_2} r^{-2} (\sin\theta)^{-1} \left[\frac{\partial}{\partial r} r^2 \sin\theta \frac{\partial}{\partial r} + \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} \right. \\ & \left. + \frac{\partial}{\partial\phi} (\sin\theta)^{-1} \frac{\partial}{\partial\phi} \right] - \frac{e^2}{4\pi\epsilon_0 r} \end{aligned} \qquad (9\text{-}37)$$

$$\begin{aligned} = {} & -\frac{\hbar^2}{2m_2} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) \right. \\ & \left. + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r}. \end{aligned} \qquad (9\text{-}38)$$

This is the same as the Hamiltonian operator given in Eq. (9-13) that was obtained by Method I.

Problem 9-2. Change coordinates in Eq. (9-1) so that the coordinates of all particles are referred to an (ξ, η, ζ) axis system parallel to the (X, Y, Z) axis system but with origin at the nuclear center of mass.

Answer. The coordinate change we are making is from the $(3l - 3)$ coordinates $(X_2, Y_2, Z_2, \ldots, Z_l)$ to the $(3l - 3)$ coordinates $(\xi_2, \eta_2, \zeta_2, \ldots, \zeta_l)$, and since this involves only Cartesian coordinates we will make the coordinate change directly in the Schrödinger equation using the chain rule (i.e., using Method I).

In the molecule, particles labeled $1, 2, \ldots, N$ are nuclei and particles labeled $N + 1, N + 2, \ldots, N + n$ are electrons; there are N nuclei, n electrons, and $N + n = l$. The (X_i, Y_i, Z_i) and (ξ_i, η_i, ζ_i) coordinates of a particle in the molecule are related by

$$\xi_i = X_i - X_{\mathrm{NCM}}, \eta_i = Y_i - Y_{\mathrm{NCM}}, \text{ and } \zeta_i = Z_i - Z_{\mathrm{NCM}}, \qquad (9\text{-}39)$$

where $(X_{\mathrm{NCM}}, Y_{\mathrm{NCM}}, Z_{\mathrm{NCM}})$ are the coordinates of the nuclear center of mass in the (X, Y, Z) axis system. If we let M_{N} be the total mass of all the nuclei in the molecule then we have

$$\xi_i = X_i + \frac{m_e}{M_{\mathrm{N}}} \sum_{r=N+1}^{l} X_r, \qquad (9\text{-}40)$$

with similar equations for η_i and ζ_i (in the following equations we will only write down the equations involving ξ_i since those involving η_i and ζ_i are then obvious). From the chain rule, Eq. (7-8), we have

$$\frac{\partial}{\partial X_r} = \sum_{i=2}^{l} \frac{\partial \xi_i}{\partial X_r} \frac{\partial}{\partial \xi_i}, \tag{9-41}$$

where $r \neq 1$, and using Eq. (9-40) this gives

$$\frac{\partial}{\partial X_r} = \sum_{i=2}^{l} \left(\delta_{ir} + \frac{m_e}{M_{\mathrm{N}}} \delta_{er} \right) \frac{\partial}{\partial \xi_i}, \tag{9-42}$$

where δ_{ir} is the Kronecker delta, and we have introduced δ_{er} which is such that $\delta_{er} = 1$ if r labels an electron (i.e., $r = N+1, N+2, \ldots, l$), and $\delta_{er} = 0$ if r labels a nucleus (i.e., $r = 2, \ldots, N$). Further application of the chain rule gives

$$\frac{\partial^2}{\partial X_r^2} = \frac{\partial^2}{\partial \xi_r^2} + \frac{2m_e}{M_{\mathrm{N}}} \delta_{er} \sum_{j=2}^{l} \frac{\partial^2}{\partial \xi_r \partial \xi_j} + \left(\frac{m_e}{M_{\mathrm{N}}} \right)^2 \delta_{er} \sum_{i,j=2}^{l} \frac{\partial^2}{\partial \xi_i \partial \xi_j}, \tag{9-43}$$

and

$$\begin{aligned} \frac{\partial^2}{\partial X_r \partial X_s} = \frac{\partial^2}{\partial \xi_r \partial \xi_s} &+ \frac{m_e}{M_{\mathrm{N}}} \left[\delta_{es} \sum_{j=2}^{l} \frac{\partial^2}{\partial \xi_r \partial \xi_j} + \delta_{er} \sum_{i=2}^{l} \frac{\partial^2}{\partial \xi_i \partial \xi_s} \right] \\ &+ \left(\frac{m_e}{M_{\mathrm{N}}} \right)^2 \delta_{er} \delta_{es} \sum_{i,j=2}^{l} \frac{\partial^2}{\partial \xi_i \partial \xi_j}, \end{aligned} \tag{9-44}$$

where r, $s \neq 1$. Summing these expressions and making use of the reductions occurring because of δ_{er} and δ_{es} we obtain (where $M = M_{\mathrm{N}} + nm_e$)

$$\sum_{r,s=2}^{l} \frac{\partial^2}{\partial X_r \partial X_s} = \left(\frac{M}{M_{\mathrm{N}}} \right)^2 \sum_{i,j=2}^{l} \frac{\partial^2}{\partial \xi_i \partial \xi_j} \tag{9-45}$$

and

$$\sum_{r=2}^{l} \frac{1}{m_r} \frac{\partial^2}{\partial X_r^2} = \sum_{i=2}^{l} \frac{1}{m_i} \frac{\partial^2}{\partial \xi_i^2} + \frac{2}{M_{\mathrm{N}}} \sum_{i=N+1}^{l} \sum_{j=2}^{l} \frac{\partial^2}{\partial \xi_i \partial \xi_j} + \frac{nm_e}{M_{\mathrm{N}}^2} \sum_{i,j=2}^{l} \frac{\partial^2}{\partial \xi_i \partial \xi_j}. \tag{9-46}$$

Combining these two equations we have

$$\begin{aligned} -\sum_{r=2}^{l} \frac{1}{m_r} \frac{\partial^2}{\partial X_r^2} &+ \frac{1}{M} \sum_{r,s=2}^{l} \frac{\partial^2}{\partial X_r \partial X_s} \\ &= -\sum_{i=2}^{l} \frac{1}{m_i} \frac{\partial^2}{\partial \xi_i^2} + \frac{1}{M_{\mathrm{N}}} \left[\sum_{i,j=2}^{N} \frac{\partial^2}{\partial \xi_i \partial \xi_j} - \sum_{i,j=N+1}^{l} \frac{\partial^2}{\partial \xi_i \partial \xi_j} \right]. \end{aligned} \tag{9-47}$$

Using this equation together with the similar ones involving the Y, Z, η, and ζ coordinates we obtain the rovibronic wave equation in this new coordinate frame as

$$[\hat{T}_{\mathrm{e}} + \hat{T}_{\mathrm{N}} + V(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}}) - E_{\mathrm{rve}}]\Phi_{\mathrm{rve}}(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}}) = 0. \qquad (9\text{-}48)$$

where

$$\hat{T}_{\mathrm{e}} = -\frac{\hbar^2}{2m_{\mathrm{e}}}\sum_{i=N+1}^{l}\nabla_i^2 - \frac{\hbar^2}{2M_{\mathrm{N}}}\sum_{i,j=N+1}^{l}\nabla_i\cdot\nabla_j, \qquad (9\text{-}49)$$

$$\hat{T}_{\mathrm{N}} = -\frac{\hbar^2}{2}\sum_{i=2}^{N}\frac{\nabla_i^2}{m_i} + \frac{\hbar^2}{2M_{\mathrm{N}}}\sum_{i,j=2}^{N}\nabla_i\cdot\nabla_j, \qquad (9\text{-}50)$$

$$\nabla_i^2 = \frac{\partial^2}{\partial\xi_i^2} + \frac{\partial^2}{\partial\eta_i^2} + \frac{\partial^2}{\partial\zeta_i^2}, \qquad (9\text{-}51)$$

$$\nabla_i\cdot\nabla_j = \frac{\partial^2}{\partial\xi_i\partial\xi_j} + \frac{\partial^2}{\partial\eta_i\partial\eta_j} + \frac{\partial^2}{\partial\zeta_i\zeta_j}, \qquad (9\text{-}52)$$

and

$$V(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}}) = \sum_{r<s=1}^{l}\frac{C_rC_se^2}{4\pi\epsilon_0R_{rs}} \qquad (9\text{-}53)$$

In Eq. (9-48), we have indicated explicitly that the electrostatic potential energy function V and the rovibronic wavefunctions Φ_{rve} depend on the nuclear coordinates $\boldsymbol{R}_{\mathrm{N}} = (\xi_2, \eta_2, \zeta_2, \xi_3, \eta_3, \zeta_3, \ldots, \xi_N, \eta_N, \zeta_N)$ and on the electronic coordinates $\boldsymbol{r}_{\mathrm{elec}} = (\xi_{N+1}, \eta_{N+1}, \zeta_{N+1}, \xi_{N+2}, \eta_{N+2}, \zeta_{N+2}, \ldots \xi_l, \eta_l, \zeta_l)$. The kinetic energy is completely separable into an electronic part $\hat{T}_{\mathrm{e}}$ and a nuclear part $\hat{T}_{\mathrm{N}}$ in these coordinates. Further, the electronic kinetic energy can be written

$$\hat{T}_{\mathrm{e}} = \hat{T}_{\mathrm{e}}^0 + \hat{T}_{\mathrm{e}}', \qquad (9\text{-}54)$$

where $\hat{T}_{\mathrm{e}}^0$ are $\hat{T}_{\mathrm{e}}'$ the first and second terms, respectively, on the right hand side of Eq. (9-49).

9.3 THE BORN-OPPENHEIMER APPROXIMATION

As discussed above, in general it is impossibly difficult to solve the rovibronic Schrödinger equation [Eq. (9-48)] without first making simplifying approximations. The most important simplification is the Born-Oppenheimer approximation. In Chapter 2 of Lefebvre-Brion and Field (1986) a good account is given for a diatomic molecule of the terms neglected in the Born-Oppenheimer approximation. In making the Born-Oppenheimer approximation we assume that the motions of the electrons are unaffected by the motions of the nuclei and, on the periodic time scale of their motion, only depend on the nuclear positions. Thus, in this approximation the wavefunctions Φ_{elec} and energies V_{elec} that describe the electronic motion are obtained from the Schrödinger equation that results after neglecting the nuclear kinetic energy term (and V_{nn}, the nuclear-nuclear repulsion part of the electrostatic potential energy V) in Eq. (9-48), i.e., from

$$[T_{\mathrm{e}}^{0} + V(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}}) - V_{\mathrm{nn}}(\boldsymbol{R}_{\mathrm{N}})]\Phi_{\mathrm{elec}}(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}}) = V_{\mathrm{elec}}(\boldsymbol{R}_{\mathrm{N}})\,\Phi_{\mathrm{elec}}(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}}), \tag{9-55}$$

where the nuclear-nuclear repulsion term is given by

$$V_{\mathrm{nn}}(\boldsymbol{R}_{\mathrm{N}}) = \sum_{\alpha<\alpha'} \frac{C_{\alpha}C_{\alpha'}e^{2}}{4\pi\epsilon_{0}R_{\alpha\alpha'}} \tag{9-56}$$

with α and α' running over the N nuclei. In Eq. (9-55), we have neglected the term T_{e}' in Eq. (9-54). It gives rise to a coupling of the electronic motions but this kinetic energy correlation term is a nuclear mass dependent contribution that is of the same order of magnitude as terms neglected in making the Born-Oppenheimer approximation. This kinetic energy coupling term can therefore be neglected in all but the most precise work where it contributes to the ***adiabatic correction*** [see Eq. (13-172)] to the Born-Oppenheimer potential energy function that we discuss below. In Eq. (9-55) the nuclear coordinates are held fixed at constant values of $\boldsymbol{R}_{\mathrm{N}}$. The Hamiltonian on the left hand side of the Schrödinger equation Eq. (9-55) describes a situation where the electrons move and the nuclei are stationary; each electron is influenced by the electrostatic fields from the other electrons and from the nuclei. The energy V_{elec} and the wavefunction Φ_{elec} depend on the chosen arrangement of the nuclei in space [defined by $\boldsymbol{R}_{\mathrm{N}}$], so that as indicated in the equation, V_{elec} and Φ_{elec} involve the nuclear coordinates $\boldsymbol{R}_{\mathrm{N}}$ as parameters. We solve Eq. (9-55) at each nuclear geometry $\boldsymbol{R}_{\mathrm{N}}$ to obtain V_{elec} and Φ_{elec}.

Using this approximation for the electronic motion we see that from the point of view of the nuclei the electronic energy V_{elec} acts as a contribution to the potential energy; the total potential in which the nuclei move is the sum of V_{elec} and V_{nn}. To move the nuclei from a configuration having $V_{\mathrm{elec}} + V_{\mathrm{nn}}$ low to one in which $V_{\mathrm{elec}} + V_{\mathrm{nn}}$ is high requires work. The Schrödinger equation for the nuclear (rotation-vibration) motion is, therefore, given by

$$\left[T_{\mathrm{N}} + V_{\mathrm{elec}}(\boldsymbol{R}_{\mathrm{N}}) + V_{\mathrm{nn}}(\boldsymbol{R}_{\mathrm{N}})\right]\Phi_{\mathrm{rv}}(\boldsymbol{R}_{\mathrm{N}}) = E_{\mathrm{rve}}^{0}\Phi_{\mathrm{rv}}(\boldsymbol{R}_{\mathrm{N}}), \tag{9-57}$$

where E_{rve}^{0} is the rovibronic energy in the Born-Oppenheimer approximation. The function $V_{\mathrm{elec}}(\boldsymbol{R}_{\mathrm{N}}) + V_{\mathrm{nn}}(\boldsymbol{R}_{\mathrm{N}})$ is called the ***Born-Oppenheimer potential energy function***. The approximate and separable rovibronic wavefunction Φ_{rve}^{0} is given by

$$\Phi_{\mathrm{rve}}^{0} = \Phi_{\mathrm{elec}}(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}})\,\Phi_{\mathrm{rv}}(\boldsymbol{R}_{\mathrm{N}}) \tag{9-58}$$

from Eqs. (9-55) and (9-57).

Alternatively, we can obtain Eq. (9-57) by inserting the wavefunction of Eq. (9-58) in Eq. (9-48) and neglecting the effect of the operator $\hat{T}_N$ on the electronic wavefunction $\Phi_{\mathrm{elec}}(\boldsymbol{R}_N, \boldsymbol{r}_{\mathrm{elec}})$. That is, with

$$\hat{T}_N\left[\Phi_{\mathrm{elec}}(\boldsymbol{R}_N, \boldsymbol{r}_{\mathrm{elec}})\Phi_{\mathrm{rv}}(\boldsymbol{R}_N)\right] = \Phi_{\mathrm{elec}}(\boldsymbol{R}_N, \boldsymbol{r}_{\mathrm{elec}})\left[\hat{T}_N\Phi_{\mathrm{rv}}(\boldsymbol{R}_N)\right] \qquad (9\text{-}59)$$

we obtain $E^0_{\mathrm{rve}} = E_{\mathrm{rve}}$, so that if Eq. (9-59) were fulfilled, the rovibronic energy obtained in the Born-Oppenheimer approximation would be the exact rovibronic energy. This equation is not fulfilled exactly because $\hat{T}_N$ involves differentiation with respect to the nuclear coordinates [Eq. (9-50)], and Φ_{elec} depends on these coordinates. The approximation inherent in Eq. (9-59) is usually acceptable for isolated ground electronic states for which the effects of the neglected terms on the molecular energies are observed experimentally only in the finer details of the isotope effects on the molecular parameters [Watson (1980)]. When electronic states are close together (compared to rotation-vibration energy separations) the Born-Oppenheimer approximation can break down severely. This will be discussed further in Chapter 13. The rotation-vibration Schrödinger equation for a bound electronic state is written so that the zero of energy is the minimum value of V_{elec}, which we call the electronic energy E_{elec}, and we have

$$[\hat{T}_N + V_N]\Phi_{\mathrm{rv}} = E_{\mathrm{rv}}\Phi_{\mathrm{rv}}, \qquad (9\text{-}60)$$

where

$$V_N = V_{\mathrm{elec}} + V_{\mathrm{nn}} - E_{\mathrm{elec}} \quad \text{and} \quad E_{\mathrm{rv}} = E^0_{\mathrm{rve}} - E_{\mathrm{elec}}. \qquad (9\text{-}61)$$

As a result of making the Born-Oppenheimer approximation we have reduced the problem of solving the $(3l-3)$-dimensional rovibronic Schrödinger equation, Eq. (9-48), to one of solving two differential equations: the electronic Schrödinger equation, Eq. (9-55), involving $3n$ electronic coordinates, and the rotation-vibration Schrödinger equation, Eq. (9-60), involving $3N-3$ nuclear coordinates. We proceed to approximate each of these equations so that they separate into soluble partial differential equations, and we obtain approximate electronic and rovibrational wavefunctions, Φ^0_{elec} and Φ^0_{rv}.

9.4 THE ELECTRONIC WAVEFUNCTIONS

9.4.1 Molecular orbitals

From Eq. (9-55) the electronic Schrödinger equation is obtained as

$$\hat{H}_{\mathrm{elec}}\Phi_{\mathrm{elec}} = V_{\mathrm{elec}}\Phi_{\mathrm{elec}}, \qquad (9\text{-}62)$$

where Φ_{elec} and V_{elec} are the eigenfunctions and eigenvalues of

$$\hat{H}_{\text{elec}} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_{i<j}\frac{e^2}{4\pi\epsilon_0 R_{ij}} - \sum_{\alpha,i}\frac{C_\alpha e^2}{4\pi\epsilon_0 R_{i\alpha}}. \tag{9-63}$$

In Eq. (9-63) i and j run over the n electrons and α runs over the N nuclei. To solve Eq. (9-62) we make approximations in order to separate the variables. If we neglect the second term in Eq. (9-63) (that is, we neglect the interaction between the electrons) we reduce $\hat{H}_{\text{elec}}$ to an approximate electronic Hamiltonian $\hat{H}^0_{\text{elec}}$ that is separable into the sum of n one-electron Hamiltonians, i.e.,

$$\hat{H}^0_{\text{elec}} = \sum_i\left\{-\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_\alpha \frac{C_\alpha e^2}{4\pi\epsilon_0 R_{i\alpha}}\right\} = \sum_i \hat{h}_i. \tag{9-64}$$

As a result of this separation of variables the eigenfunctions and eigenvalues of $\hat{H}^0_{\text{elec}}$ are formally given as

$$\Phi^{(\text{p})}_{\text{elec}} = \phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2)\cdots\phi_\lambda(\boldsymbol{r}_n) \tag{9-65}$$

and

$$V^0_{\text{elec}} = \varepsilon_a + \varepsilon_b + \cdots + \varepsilon_\lambda, \tag{9-66}$$

where

$$\hat{h}\phi_k(\boldsymbol{r}) = \varepsilon_k\phi_k(\boldsymbol{r}), \tag{9-67}$$

and $\boldsymbol{r}$ are the electronic coordinates in the (ξ,η,ζ) axis system. The superscript (p) in $\Phi^{(\text{p})}_{\text{elec}}$ indicates that this function is obtained as a *product* of the one-electron functions $\phi_k(\boldsymbol{r})$. The $\phi_k(\boldsymbol{r})$ and the ε_k depend on the nuclear coordinates but this is not put in explicitly to avoid complicating the expressions. The eigenfunctions $\phi_k(\boldsymbol{r})$ and eigenvalues ε_k of $\hat{h}$ are called *molecular orbitals* (*MO's*) and *molecular orbital energies*, respectively. To determine them we solve Eq. (9-67) for the motion of an electron in the electrostatic field of a given arrangement of the nuclei.

9.4.2 Electron spin and the Slater determinant

The above electron orbital functions can be combined with electron spin functions to form appropriate basis functions. An electron has a spin of 1/2 and its projection quantum number takes the values ±1/2; the two possible spin functions for an electron are written $\alpha(\sigma) = |\frac{1}{2},\frac{1}{2}\rangle$ and $\beta(\sigma) = |\frac{1}{2},-\frac{1}{2}\rangle$, respectively, where σ is the *spin coordinate* of the electron. In order to impose the Pauli exclusion principle (see page 139) some *ab initio* methods for solving Eq. (9-62) [see, for example, Hehre, Radom, Schleyer, and Pople (1986), or

Hinchcliffe (1988)] use an electronic basis wavefunction given by the *Slater determinant* [Slater (1929)]

$$\Phi^0_{\rm elec}(r_1, \sigma_1, r_2, \sigma_2, \ldots, r_n, \sigma_n)$$
$$= \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_a(r_1)\alpha(\sigma_1) & \phi_a(r_1)\beta(\sigma_1) & \phi_b(r_1)\alpha(\sigma_1) & \ldots & \phi_\lambda(r_1)\beta(\sigma_1) \\ \phi_a(r_2)\alpha(\sigma_2) & \phi_a(r_2)\beta(\sigma_2) & \phi_b(r_2)\alpha(\sigma_2) & \ldots & \phi_\lambda(r_2)\beta(\sigma_2) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \phi_a(r_n)\alpha(\sigma_n) & \phi_a(r_n)\beta(\sigma_n) & \phi_b(r_n)\alpha(\sigma_n) & \ldots & \phi_\lambda(r_n)\beta(\sigma_n) \end{vmatrix}, \tag{9-68}$$

where σ_i is the spin coordinate of electron i, and the $\phi_k(r_i)$ are the electron orbital functions from Eqs. (9-65) to (9-67). Alternative so-called spin-free techniques that do not use Slater determinants are discussed in Section 9.4.5. The interchange of two rows of the determinant in Eq. (9-68) is equivalent to the exchange of the spatial coordinates r_i and the spin coordinates σ_i of two of the electrons in the set 1, 2, 3, ..., n. From the properties of determinants [see Eq. (5-13)] this will cause the function to change its sign and the Pauli exclusion principle is thus satisfied. We note also that a given molecular orbital $\phi_k(r)$ can occur at most twice in the Slater determinant. If it occurs twice [in which case we say that it is *doubly occupied*], it must occur once multiplied by the α spin function and once multiplied by the β spin function. If we attempt to let a molecular orbital be triply occupied in a Slater determinant, it would be necessary to have the orbital occur twice multiplied by α, or twice multiplied by β. The resulting determinant would have two identical columns, and such a determinant has the value zero and cannot be used to represent the electronic wavefunction. Such states are excluded by the Pauli exclusion principle.

We can easily show that the Slater determinant $\Phi^0_{\rm elec}$ is an eigenfunction of $\hat{H}^0_{\rm elec}$ given in Eq. (9-64). The determinant is a linear combination of $n!$ orbital products of the type given in Eq. (9-65); each of these products is an eigenfunction of $\hat{H}^0_{\rm elec}$, and all products correspond to the same eigenvalue, the sum of molecular orbital energies given by Eq. (9-66). We take the Slater determinant as our zero order approximation of the electronic wavefunction. The one-electron products $\phi_k(r)\alpha(\sigma)$ and $\phi_k(r)\beta(\sigma)$ are called *spin-orbitals*. We describe the wavefunction $\Phi^0_{\rm elec}$ in Eq. (9-68) as the electron *configuration* having, for example, two electrons in orbital ϕ_a, two electrons in orbital ϕ_b, and so on. It is evident that $\Phi^0_{\rm elec}$ in Eq. (9-68) will transform according to the Pauli allowed irreducible representation $\Gamma^{(e)}(A)$ in the Electron Permutation Group $S_n^{(e)}$ [see Chapter 7].

The approximation made in obtaining Eqs. (9-66) and (9-68) as solutions to Eq. (9-62) is drastic. The second term in Eq. (9-63) represents the mutual electrostatic repulsion of the electrons, and this has a large modifying effect on the electronic energies and wavefunctions. As a result of it the motions of the electrons are not independent of each other, as they would be if described by $\Phi^0_{\rm elec}$ in Eq. (9-68); the motions of the electrons are *correlated*. However, the eigenfunctions $\Phi^0_{\rm elec}$ are useful for making a symmetry classification of the eigenfunctions of $\hat{H}_{\mathrm{elec}}$ and for describing them [see Chapter 12].

9.4.3 Self consistent field calculations

The theoretical method outlined here, in which we neglect completely the electron-electron interaction represented by the second term in Eq. (9-63), is referred to as the *independent particle model*. We can improve the description of the electronic motion relative to the independent particle model by making a so-called *Self Consistent Field (SCF)* [or *Hartree-Fock (HF)*] calculation. In an SCF calculation, we take the electronic wavefunction $\Phi_{\mathrm{elec}}^{\mathrm{SCF}}$ to be represented by a single Slater determinant [Eq. (9-68)]. The molecular orbitals $\phi_k(\boldsymbol{r})$ used in constructing the Slater determinant are expanded in terms of basis functions $\chi_\mu(\boldsymbol{r})$:

$$\phi_k(\boldsymbol{r}) = \sum_{\mu=1}^{N_b} c_{\mu k}\, \chi_\mu(\boldsymbol{r}), \tag{9-69}$$

where the $c_{\mu k}$ are expansion coefficients to be determined in the SCF calculation. We say that we write the molecular orbital $\phi_k(\boldsymbol{r})$ as LCAO's [Linear Combinations of Atomic Orbitals].

The basis functions $\chi_\mu(\boldsymbol{r})$ can, for example, be chosen as *Slater-type orbitals* (STO's); these functions are very similar to the eigenfunctions of a one-electron atom and are labeled in the same way: $1s$, $2s$, $2p_x$, etc. The first three Slater-type orbitals are given by

$$\chi_{1s}\left(r^{(\alpha)}\right) = \sqrt{\frac{\zeta_1^3}{\pi}} \exp\left(-\zeta_1 r^{(\alpha)}\right), \tag{9-70}$$

$$\chi_{2s}\left(r^{(\alpha)}\right) = \sqrt{\frac{\zeta_2^5}{96\pi}}\, r^{(\alpha)} \exp\left(-\zeta_2 r^{(\alpha)}/2\right) \tag{9-71}$$

and

$$\chi_{2p_x}\left(r^{(\alpha)}\right) = \sqrt{\frac{\zeta_2^5}{32\pi}}\, x^{(\alpha)} \exp\left(-\zeta_2 r^{(\alpha)}/2\right). \tag{9-72}$$

In these equations, the coordinates $(x^{(\alpha)}, y^{(\alpha)}, z^{(\alpha)})$ refer to an axis system with axes parallel to the (ξ, η, ζ) system but with origin in nucleus α;

$$r^{(\alpha)} = \sqrt{\left(x^{(\alpha)}\right)^2 + \left(y^{(\alpha)}\right)^2 + \left(z^{(\alpha)}\right)^2}.$$

These coordinates are appropriate for a Slater-type orbital localized on nucleus α. The STO's contain the parameters ζ_1, ζ_2, etc., which are held constant during the SCF calculation. Their values for different elements are found in basis set "recipes" given in the *ab initio* literature [see, for example, Dunning and Hay (1977) or Huzinaga (1984)]; these parameters have been optimized in some way, for example in an SCF calculation for a free atom of the element in question. In such a calculation, the basis functions $\chi_\mu(\boldsymbol{r})$ are taken to be the atomic orbitals used in constructing a Slater determinant to represent the electronic wavefunction for the atom, and the basis set parameters are obtained as described below to give the best description of the electronic motion.

The most used basis functions are *Gauss-type orbitals (GTO's)* (or *Gaussian orbitals*) [Gaussian functions were introduced by Boys (1950)]. A general GTO localized on nucleus α is given by

$$g_{n_x n_y n_z}\left(\boldsymbol{r}^{(\alpha)}, \zeta_{\mathrm{GTO}}\right) = N_{n_x n_y n_z}\left(x^{(\alpha)}\right)^{n_x}\left(y^{(\alpha)}\right)^{n_y}\left(z^{(\alpha)}\right)^{n_z} \\ \times \exp\left[-\zeta_{\mathrm{GTO}}\left(r^{(\alpha)}\right)^2\right], \tag{9-73}$$

where n_x, n_y, n_z are non-negative integers, $N_{n_x n_y n_z}$ is a normalization constant, and ζ_{GTO} is a parameter. The Gauss-type orbitals with $n_x = n_y = n_z = 0$ are called *s*-orbitals, those with $n_x + n_y + n_z = 1$ are called *p*-orbitals, those with $n_x + n_y + n_z = 2$ are called *d*-orbitals, and so on. From a physical point of view these function are less suitable basis functions than the STO's, because they are less similar to the eigenfunctions of a one-electron atom, but the GTO's allow certain integrals needed in the SCF calculation (see below) to be calculated in a much simpler and more efficient way than by use of STO's.

The so-called "contracted Gaussians" constitute a third possibility for choosing the basis functions $\chi_\mu(\boldsymbol{r}_r)$. These functions are defined as linear combinations of the "primitive Gaussians" given in Eq. (9-73):

$$\chi_\mu(\boldsymbol{r}^{(\alpha)}) = \sum_{n_x n_y n_z} d^{(\mu)}_{n_x n_y n_z} g_{n_x n_y n_z}\left(\boldsymbol{r}^{(\alpha)}, \zeta_{\mathrm{GTO}}\right) \tag{9-74}$$

The coefficients $d_{n_x n_y n_z}$ [and the "exponents" ζ_{GTO}] are not varied in the SCF calculation; they are kept fixed at "standard" values that can be found in the *ab initio* literature. For example, the coefficients can be chosen so that the function in Eq. (9-74) approximates a Slater type orbital as closely as possible.

In carrying out the SCF calculation, we make use of the *variation principle* [see, for example, Hinchcliffe (1988) or Szabo and Ostlund (1982)]. The variation principle says that if $V_{\mathrm{elec}}^{\mathrm{GS}}$ is the exact eigenvalue of the Schrödinger equation in Eq. (9-62) for the electronic ground state [i.e., $V_{\mathrm{elec}}^{\mathrm{GS}}$ is the smallest eigenvalue that solves Eq. (9-62)], then for an arbitrarily chosen trial electronic wavefunction $\Phi_{\mathrm{elec}}^{(\mathrm{trial})}$ we have

$$\left\langle \Phi_{\mathrm{elec}}^{(\mathrm{trial})} \middle| \hat{H}_{\mathrm{elec}} \middle| \Phi_{\mathrm{elec}}^{(\mathrm{trial})} \right\rangle \geq V_{\mathrm{elec}}^{\mathrm{GS}}. \tag{9-75}$$

The expectation value on the left hand side of Eq. (9-75) will be equal to $V_{\mathrm{elec}}^{\mathrm{GS}}$ if and only if the trial wavefunction $\Phi_{\mathrm{elec}}^{(\mathrm{trial})} = \Phi_{\mathrm{elec}}^{\mathrm{GS}}$, the eigenfunction of $\hat{H}_{\mathrm{elec}}$ corresponding to the eigenvalue $V_{\mathrm{elec}}^{\mathrm{GS}}$. In the SCF calculation we take the trial wavefunction $\Phi_{\mathrm{elec}}^{(\mathrm{trial})}$ to be a Slater determinant Φ_{elec}^{0} [Eq. (9-68)] constructed from molecular orbitals that are expanded as given in Eq. (9-69). Since we know from Eq. (9-75) that the smallest attainable value of the expectation value $\left\langle \Phi^0_{\mathrm{elec}} \middle| \hat{H}_{\mathrm{elec}} \middle| \Phi^0_{\mathrm{elec}} \right\rangle$ will give the best approximation for the energy of the electronic ground state, we then determine the expansion coefficients $c_{\mu k}$ [$\mu = 1, 2, 3, \ldots, N_{\mathrm{b}}$; $k = 1, 2, 3, \ldots, \lambda$] of Eq. (9-69) so as to minimize this expectation value.

In order for the expectation value $\left\langle \Phi^0_{\mathrm{elec}} \middle| \hat{H}_{\mathrm{elec}} \middle| \Phi^0_{\mathrm{elec}} \right\rangle$ to attain its minimum value, with the set of molecular orbitals $\phi_k(\boldsymbol{r})$ [Eq. (9-69)] being normalized and orthogonal, the set of expansion coefficients $c_{\mu k}$ must fulfill the ***Roothaan-Hall equations***

$$\sum_{\nu=1}^{N_{\mathrm{b}}} (F_{\mu\nu} - \epsilon_k S_{\mu\nu})\, c_{\nu k} = 0, \quad \mu = 1, 2, \ldots, N_{\mathrm{b}}. \tag{9-76}$$

Here, $F_{\mu\nu}$ is an element of the $N_{\mathrm{b}} \times N_{\mathrm{b}}$ ***Fock matrix***. If, for example, we have an even number of electrons $n = 2\lambda$, and the Slater determinant used as a trial function has λ doubly occupied orbitals $\phi_1, \phi_2, \phi_3, \ldots, \phi_\lambda$ [that is, each of these λ orbitals is used twice in the Slater determinant, once with α spin and once with β spin], then the Fock matrix elements are given by

$$F_{\mu\nu} = H^{\mathrm{core}}_{\mu\nu} + \sum_{\mu'=1}^{N_{\mathrm{b}}} \sum_{\nu'=1}^{N_{\mathrm{b}}} P_{\mu'\nu'} \left\{ (\mu\nu|\mu'\nu') - \frac{1}{2}(\mu\nu'|\mu'\nu) \right\}, \tag{9-77}$$

with the ***density matrix element***

$$P_{\mu\nu} = 2 \sum_{k=1}^{\lambda} c^*_{\mu k} c_{\nu k}, \tag{9-78}$$

the ***one-electron integral***

$$H^{\mathrm{core}}_{\mu\nu} = \int \chi_\mu(\boldsymbol{r})^* \hat{h} \chi_\nu(\boldsymbol{r})\, d\xi\, d\eta\, d\zeta \tag{9-79}$$

and the ***two-electron integral***

$$(\mu\nu|\mu'\nu') = \int\!\!\int \frac{e^2\, \chi_\mu(\boldsymbol{r}_1)^* \chi_{\mu'}(\boldsymbol{r}_2)^* \chi_\nu(\boldsymbol{r}_1) \chi_{\nu'}(\boldsymbol{r}_2)}{4\pi\epsilon_0 \sqrt{(\xi_1 - \xi_2)^2 + (\eta_1 - \eta_2)^2 + (\zeta_1 - \zeta_2)^2}} \times d\xi_1 d\eta_1 d\zeta_1 d\xi_2 d\eta_2 d\zeta_2. \tag{9-80}$$

With a basis set of Slater-type orbitals, the computation of the two-electron integrals in Eq. (9-80) is very cumbersome, whereas it can be carried out rather efficiently in a basis set of Gauss-type orbitals. This is the reason for the success of Gauss-type orbitals as basis functions in SCF calculations. Finally, the ***overlap integral*** $S_{\mu\nu}$ in Eq. (9-76) is given by

$$S_{\mu\nu} = \int \chi_\mu(\boldsymbol{r}_i)^* \chi_\nu(\boldsymbol{r}_i)\, d\xi_i\, d\eta_i\, d\zeta_i. \tag{9-81}$$

The Roothaan-Hall equations in Eq. (9-76) have the same analytical form as the eigenvalue problem of Eq. (6-158). [In Eq. (6-158), we have $S_{mn} = \delta_{mn}$ because the basis set employed is normalized and orthogonal; the basis functions $\chi_\mu(\boldsymbol{r})$ used here are not necessarily mutually orthogonal.] Thus, the expansion coefficients $c_{\mu k}$ are formally the components of the eigenvectors of the Fock matrix. We cannot, however, simply solve Eq. (9-76) as an eigenvalue problem because the Fock matrix elements depend on the expansion coefficients $c_{\mu k}$ through the density matrix elements $P_{\mu'\nu'}$ [Eqs. (9-77) and (9-78)], and so we resort to an iterative procedure.

The quantities $H_{\mu\nu}^{\mathrm{core}}$, $(\mu\nu|\mu'\nu')$, and $S_{\mu\nu}$ depend on known operators and known basis functions $\chi_\mu(\boldsymbol{r})$; they can be calculated once and for all and stored for later use at the beginning of the SCF calculation. We guess a set of starting values for the expansion coefficients $c_{\mu k}$. These starting values could, for example, be obtained from an SCF calculation carried out at a neighboring nuclear geometry, but if no such results are available, it will often be sufficient to set all $c_{\mu k} = 0$ in this initial step. With the set of starting values for the $c_{\mu k}$, we can calculate values for the Fock matrix elements $F_{\mu\nu}$ from Eqs. (9-77) and (9-78) and insert these in the Roothaan-Hall equations (9-76). With these values of $F_{\mu\nu}$, the Roothaan-Hall equations constitute a standard eigenvalue problem which we can solve to obtain values of the ϵ_k and the $c_{\mu k}$. These new values of the $c_{\mu k}$ will not be equal to our starting values [if they were, we would have had the incredible luck to guess a set of solutions right away], and so we insert them in Eqs. (9-77) and (9-78) to obtain new values for the Fock matrix element, we insert these in Eq. (9-76) and solve to obtain new values for the ϵ_k and the $c_{\mu k}$. If we keep repeating this procedure, the $c_{\mu k}$ will eventually become ***self-consistent*** in the sense that they do not change when we run further cycles of the iteration. The self-consistent expansion coefficients $c_{\mu k}$, with their associated orbital energies ϵ_k, obviously constitute the solutions of the Roothaan-Hall equations. Once self-consistency has been obtained, the SCF approximation to the energy of the electronic ground state, $V_{\mathrm{elec}}^{\mathrm{SCF}}$, can be computed as

$$V_{\mathrm{elec}}^{\mathrm{SCF}} = \frac{1}{2}\sum_{\mu=1}^{N_b}\sum_{\nu=1}^{N_b} P_{\mu\nu}\left(F_{\mu\nu} + H_{\mu\nu}^{\mathrm{core}}\right). \tag{9-82}$$

In order to obtain the total Born-Oppenheimer potential energy function V_{N} to be used in Eq. (9-60), we add to V_{elec} the term V_{nn} defined in Eq. (9-56).

Compared to the independent particle model, the SCF theory to some extent accounts for the energy associated with electron-electron interaction since the second term in Eq. (9-63), which represents the potential energy resulting from electrostatic interaction between the electrons, has been taken into account in the calculation of the expectation value $\left\langle \Phi_{\mathrm{elec}}^0 \middle| \hat{H}_{\mathrm{elec}} \middle| \Phi_{\mathrm{elec}}^0 \right\rangle$ minimized in the SCF calculation. This term gives rise to the integrals $(\mu\nu|\mu'\nu')$ of Eq. (9-81). Thus the SCF theory is a significant improvement over the independent particle model. However, the SCF description of the electron-electron interaction is incomplete. We are using a single Slater determinant to represent the electronic wavefunction, and this form of the wavefunction is only appropriate for non-interacting particles.

We can improve the SCF solution by increasing the number of basis functions $\chi_\mu(\boldsymbol{r})$ used in the self-consistent field equations; using a complete set of basis functions leads to the so-called *Hartree-Fock limit*.

9.4.4 Configuration interaction calculations

The simplest possible way, from a formal point of view, of obtaining better solutions to Eq. (9-62) is to carry out *Configuration Interaction (CI) calculations*. We first note that the solution of the Roothaan-Hall equations (9-76) will, of necessity, produce N_b different eigenvectors of the Fock matrix, $(c_{1k}, c_{2k}, c_{3k}, \ldots, c_{N_b k})$, $k = 1, 2, 3, \ldots, N_b$. Each eigenvector defines one molecular orbital [Eq. (9-69)], and so the SCF calculation provides us with N_b different molecular orbitals. However, in order to construct the one Slater determinant that represents the electronic ground state wavefunction in the SCF theory, we normally need far fewer orbitals. For example, for an even number of electrons $n = 2\lambda$ we only need the λ orbitals with the lowest values of ϵ_k to construct the Slater determinant if we let each orbital be doubly occupied, and in a realistic SCF calculation we choose $N_b \gg \lambda$. The orbitals required to construct the Slater determinant representing the electronic ground state wavefunction are called *occupied orbitals*; the "superfluous" orbitals that do not appear in this determinant are called *virtual orbitals*. We use the virtual orbitals to construct *substituted determinants* from the single SCF determinant representing the electronic ground state wavefunction. A substituted determinant, $\Phi_{\text{elec}}^{\text{SCF},q}$ say [where q is an index labeling the substitutions], is obtained from the SCF determinant by replacing a number of occupied orbitals $\phi_i(\boldsymbol{r})$, $\phi_j(\boldsymbol{r})$, $\phi_k(\boldsymbol{r})$, ... by the same number of virtual orbitals $\phi_a(\boldsymbol{r})$, $\phi_b(\boldsymbol{r})$, $\phi_c(\boldsymbol{r})$, ... We speak about *single substitutions*, *double substitutions*, *triple substitutions*, etc., depending on how many occupied orbitals we have replaced by virtual orbitals.

In a CI calculation, we construct the matrix representation of the electronic Hamiltonian $\hat{H}_{\text{elec}}$ in a basis of substituted determinants and diagonalize this matrix as described in Eqs. (6-145)-(6-162). That is, in the CI theory we represent the electronic wavefunction as a superposition of Slater determinants

$$\Phi_{\text{elec}}^{\text{CI},n} = \sum_{q=1}^{p} a_{nq} \Phi_{\text{elec}}^{\text{SCF},q}, \tag{9-83}$$

where n is an index numbering the CI solutions, and the coefficients a_{nq}, and the energies $V_{\text{elec}}^{\text{CI},n}$, are obtained from the diagonalization of the matrix representation of $\hat{H}_{\text{elec}}$. With N_b molecular orbitals available, we can construct a finite number of substituted determinants. If we use all these determinants in constructing the matrix representation of $\hat{H}_{\text{elec}}$ to be diagonalized, we say that we are carrying out a *full CI* calculation. Owing to computer limitations full CI calculations will only be feasible for molecules with very few electrons.

Normally, we make *limited CI* calculations in which we use only a subset of all the determinants that could be constructed. There exist many computational methods for carrying out limited CI calculations; they differ mainly in the strategies employed for selecting, among all the possible substituted determinants, "important" determinants to be included in the summation of Eq. (9-83). Obviously, in order to do a CI calculation we must first do an SCF calculation. Therefore, the two calculations are often referred to as one *SCF-CI calculation*. We note that the CI wavefunction $\Phi_{\mathrm{elec}}^{\mathrm{CI},n}$ will necessarily transform according to the Pauli allowed irreducible representation $\Gamma^{(e)}(\mathrm{A})$ in the Electron Permutation Group $\boldsymbol{S}_n^{(e)}$. This is a trivial consequence of the fact that all the Slater determinants $\Phi_{\mathrm{elec}}^{\mathrm{SCF},q}$ transform according to this representation.

The lowest calculated CI energy, $V_{\mathrm{elec}}^{\mathrm{CI},0}$ say, is necessarily larger than the true energy of the electronic ground state $V_{\mathrm{elec}}^{\mathrm{GS}}$. This is a consequence of the variation principle. Equation (9-75) holds also if we take the the trial wavefunction to be the CI wavefunction $\Phi_{\mathrm{elec}}^{\mathrm{CI},0}$ for the electronic ground state. However, if we number the CI energies [i.e., the eigenvalues of the matrix representation of $\hat{H}_{\mathrm{elec}}$ in the basis of substituted determinants] $V_{\mathrm{elec}}^{\mathrm{CI},0}$, $V_{\mathrm{elec}}^{\mathrm{CI},1}$, $V_{\mathrm{elec}}^{\mathrm{CI},2}$, ... in ascending order, $V_{\mathrm{elec}}^{\mathrm{CI},n}$ will be larger or equal to the true energy of the n'th excited state and will thus provide an approximate value for this energy. This is *MacDonald's theorem* [MacDonald (1933)].

We will denote an electronic wavefunction as $\Phi_{\mathrm{elec}}^{(e,S,m_S)}$. The function could be an eigenfunction of $\hat{H}_{\mathrm{elec}}$ obtained in an SCF-CI calculation as described above, or it could be obtained by another method. We label the eigenfunction by S (the quantum number specifying the total electron spin angular momentum of the state) and m_S (the quantum number specifying the space fixed projection of the total electron spin angular momentum). We can do this since the operators $\hat{\boldsymbol{S}}^2$ (the square of the total electron spin angular momentum) and $\hat{S}_\zeta$ (the ζ component of the total electron spin) commute with $\hat{H}_{\mathrm{elec}}$ [see Eqs. (10-95) and (10-96)]. The index e numbers the electronic states with given (S, m_S) values. The *multiplicity*, or spin degeneracy, of an electronic state is $2S + 1$; for $S = 0$ we have a *singlet state*, for $S = 1/2$ we have a *doublet state*, for $S = 1$ we have a *triplet state*, and so on.

In practical *ab initio* calculations, the input data are the Cartesian (ξ, η, ζ) coordinates of the nuclei [i.e., the components of the vector $\boldsymbol{R}_{\mathrm{N}}$]. These coordinates are customarily given in *atomic units*. The atomic unit of length is the *bohr*

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}, \tag{9-84}$$

where $a_0 \approx 5.3 \times 10^{-11}$ m. The result of an *ab initio* calculation will be a value of the Born-Oppenheimer potential energy function $V_{\mathrm{elec}} + V_{\mathrm{nn}}$, and this quantity will normally be expressed in atomic units of energy. The atomic unit of energy is the *hartree*

$$E_\mathrm{h} = \frac{e^2}{4\pi\epsilon_0 a_0}, \tag{9-85}$$

where $E_\mathrm{h} \approx 4.4 \times 10^{-18}$ J, or $E_\mathrm{h}/(hc) \approx 2.2 \times 10^5\ \mathrm{cm}^{-1}$ (c is the speed of light in vacuum). The computed value of $V_\mathrm{elec} + V_\mathrm{nn}$ is the energy measured relative to a situation in which all of the particles (nuclei and electrons) in the molecule are stationary and at an infinite distance from each other. The electronic Schrödinger equation, Eq. (9-62), does not explicitly involve the fundamental constants $\hbar$, m_e, and e, when it is expressed in atomic units.

The SCF-CI technique yields results [i.e., potential energy curves V_N] that are very close to the experimentally derived quantities for small molecules. In order to solve the electronic Schrödinger equation Eq. (9-62) exactly the SCF-CI calculation would have to be taken to two limits: (a) We must reach the Hartree-Fock limit in the SCF part of the calculation, meaning that we must allow for infinitely many basis functions in the expansion of Eq. (9-69), and (b) We must do a full CI calculation with the infinitely many substituted determinants resulting from the SCF calculation, i.e., we must allow for infinitely many terms in the expansion of Eq. (9-83). In actual calculations we will fall short of both limits.

A recent review of CI theory by Shavitt (1998) points out that the CI method has important limitations. One problem is its very slow convergence. Shavitt (1998) states that in recent years CI has been supplanted to a considerable extent by modern many-body methods, particularly coupled cluster methods [CCSD, CCSD(T), CCSDT]. Reviews of coupled cluster theory are given by Scuseria and Lee (1995), Bartlett (1995), and Gauss (1998). As discussed by Noga, Klopper and Kutzelnigg (1997), one important reason for the slow convergence of a CI calculation is that the analytical form of the electronic wavefunction given by Eq. (9-83) has difficulty describing the volume of configuration space in the vicinity of a point where two electrons have the same spatial coordinates. Around such a point, the wavefunction forms a so-called "cusp" which cannot be easily mimicked by the SCF-CI wavefunction. In order to obtain faster convergence of the CI calculation, other analytical forms for the wavefunction have been suggested. One such method, which has proved successful for small molecules [see, for example, Klopper, Quack, and Suhm (1996)] is the so-called CC-R12 method, which introduces terms explicitly depending on electron-electron distances in the analytical expression for the wavefunction. For a two-electron molecule the CC-R12 method would replace Eq. (9-83) by the unnormalized wavefunction

$$\Phi_\mathrm{elec}^{\mathrm{CC\text{-}R12},n} = \frac{r_{12}}{a_0}\Phi_\mathrm{elec}^{\mathrm{SCF},q'} + \sum_q a_{nq}\Phi_\mathrm{elec}^{\mathrm{SCF},q}, \tag{9-86}$$

where one selected Slater determinant $\Phi_\mathrm{elec}^{\mathrm{SCF},q'}$ is multiplied by r_{12}, the distance between the two electrons.

9.4.5 Electron permutation groups and Young tableau

As far as nuclear permutation symmetry is concerned we rarely set up and use complete nuclear permutation groups, preferring instead to use the MS group for the reasons discussed in Chapter 3. However, in the *symmetric group* approach to performing CI calculations the complete electron permutation group $\boldsymbol{S}_n$ for a molecule with n electrons is used. This group is called the *symmetric* group; see Chapter 13 of Wigner (1959). The symmetric group approach is one of the ways of solving large scale configuration interaction calculations of electronic wavefunctions, and in it the basis states are labeled using the irreducible representations of the symmetric group. In this technique one does not use Slater determinants but orbital and spin basis functions are formally built up separately in a way that ensures that both bases generate irreducible representations of the symmetric group (the spin functions also being eigenfunctions of $\hat{\boldsymbol{S}}^2$ and $\hat{S}_\zeta$). In principle these functions are combined to form spin-orbital functions that have the symmetry $\Gamma^{(e)}(\mathrm{A})$ [see Table 7-3]. Two representations of the symmetric group whose product contains $\Gamma^{(e)}(\mathrm{A})$ are said to be "associate" or "dual" (they must be of the same dimension). In fact by using these ideas appropriately one does not actually ever need to construct the spin functions since the orbital functions are formed in the appropriate way for the multiplicity of the state under consideration; the spin is carried along by implication. In this way one gets a spin-free or spin-adapted formalism that greatly simplifies the problem. The study of how to set up this spin-adapted formalism using the symmetric group forms a field rather like angular momentum theory; it has an appealing self-contained algebra, and laborious calculations can be simplified by using it in an appropriate way. To delve deeply into this subject would take us too far from the scope of the book. However, the symmetric group approach does involve molecular symmetry and permutations (albeit permutations of the electrons), so some discussion is warranted. Also as larger and larger weakly bound cluster molecules are studied with rotational resolution, it will become necessary to use very large MS groups for the analysis of the spectrum (see, for example, the ammonia dimer discussed in Section 16.5.2). It may be that some of the techniques used in the symmetric group approach to the CI problem are of use in dealing with the nuclear permutation symmetry of rovibronic states in such cases. A comprehensive treatment of the use of the symmetric group in quantum chemistry studies of atoms, molecules and solids is given by Pauncz (1995).

It all starts from the observation that the class structure of a symmetric group can be determined by inspection since all permutations of the same shape (i.e., consisting of the same number of independent transpositions, independent cycles of three, independent cycles of four, etc.) are in the same class (see Section 5.6); the proof of this is left as an exercise for the reader. For example the 120 elements of the symmetric group $\boldsymbol{S}_5$ divide up into seven classes, and the elements in these classes have the following shapes:

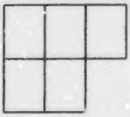
$$E, (xx), (xx)(xx), (xxx), (xxx)(xx), (xxxx), \text{and } (xxxxx). \tag{9-87}$$

The number of classes in the symmetric group $\boldsymbol{S}_n$ is given by the *partition number* of n, i.e., the number of ways of writing n as the sum of integers. For example, for $n = 5$ we can write

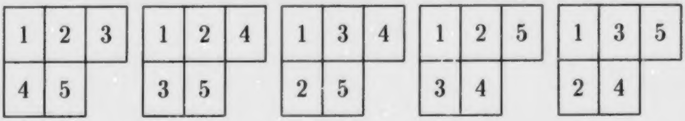
$$\begin{aligned} 5 = {} & 1+1+1+1+1,\ 2+1+1+1,\ 2+2+1,\ 3+1+1, \\ & 3+2,\ 4+1,\ \text{or } 5, \end{aligned} \tag{9-88}$$

so that the partition number of 5 is 7. The parallel between this partitioning of the number 5 and the shapes of the permutations in each class in Eq. (9-87) is obvious. Since the number of irreducible representations in a group is equal to the number of classes we can immediately deduce the number of irreducible representations in $\boldsymbol{S}_n$ once we have the partition number of n. For example, the group $\boldsymbol{S}_5$ has seven irreducible representations.

Based on the partitioning of the number n we can introduce *Young tableau*. The fifth partition in Eq. (9-87) [i.e., $(xxx)(xx)$] is called [3,2] and it can be written in the form of a *Young diagram* (or 'shape' or 'pattern'):



If we assign the numbers 1, 2, ... n in any order to the boxes in a Young diagram we obtain a Young tableau; the *standard tableau* are obtained if the numbers are in ascending order going from left to right and going from top to bottom. The complete set of standard tableau for $n = 5$ and partition [3,2] are



where they are ordered according to the *last-letter sequence*; in this order they are named $\mathrm{T}_1^{[3,2]}, \mathrm{T}_2^{[3,2]}, \ldots, \mathrm{T}_{r_{\max}}^{[3,2]}$ (where $r_{\max} = 5$ for [3,2]), respectively. The "last-letter" in this example is the number 5, and the "last-letter sequence" is determined according to the following prescription: we order the tableau so that those with 5 in the last position in the last row come before those with 5 in the last position of the penultimate row; those with 5 in the last position in the last row are ordered with respect to the position of 4, and so on.

The standard tableau are of importance because each partition can be put into correspondence with an irreducible representation of $\boldsymbol{S}_n$ (the number of standard tableau, $r_{\max}$, for that partition gives the dimension of the related irreducible representation). A simple notation for the irreducible representations of $\boldsymbol{S}_n$, based on the partition to which it corresponds, is used; for example, the irreducible representation of $\boldsymbol{S}_5$ that corresponds to the above standard tableau is called $\boldsymbol{D}_{[3,2]}$. Irreducible representations that are the dual of each other [i.e., that multiply together to give a representation containing $\Gamma^{(e)}(\mathrm{A})$] have standard tableau that are the 'transpose' of each other.

As an example of the relationships that can be visualized using the tableau we consider the correlation of $\boldsymbol{D}_{[3,2]}$ to the irreducible representations of the subgroup $\boldsymbol{S}_4$. This correlation (or ***subduction***) is given by

$$\boldsymbol{D}_{[3,2]} \rightarrow \boldsymbol{D}_{[3,1]} \oplus \boldsymbol{D}_{[2,2]}. \tag{9-89}$$

and it can be deduced by deleting the 5-box from each $T_r^{[3,2]}$. $\boldsymbol{D}_{[3,1]}$ in $\boldsymbol{S}_4$ corresponds to the tableau

$$\begin{array}{|c|c|c|}\hline 1 & 2 & 3 \\ \hline 4 \\ \cline{1-1}\end{array} \quad \begin{array}{|c|c|c|}\hline 1 & 2 & 4 \\ \hline 3 \\ \cline{1-1}\end{array} \quad \begin{array}{|c|c|c|}\hline 1 & 3 & 4 \\ \hline 2 \\ \cline{1-1}\end{array}$$

and $\boldsymbol{D}_{[2,2]}$ in $\boldsymbol{S}_4$ corresponds to the tableau

$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 4 \\ \hline\end{array} \quad \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 & 4 \\ \hline\end{array}$$

This type of connection forms an important part of the algebra of the tableau and of the related irreducible representations. It becomes possible to classify functions of given permutational symmetry according to chains of irreducible representations using the subduction $\boldsymbol{S}_n \rightarrow \boldsymbol{S}_{n-1} \rightarrow \ldots \rightarrow \boldsymbol{S}_1$. Such a "genealogical" classification is valuable in CI calculations when vast numbers of configuration functions need to be sorted and processed. An important aspect of this work is the construction of appropriate projection operators (see Section 6.3), called ***Young operators***, that are special linear combinations of the permutations in the group chosen to generate a function that transforms irreducibly when they act on an arbitrary function.

The character tables of the $\boldsymbol{S}_2$ and $\boldsymbol{S}_4$ groups are given in Table 5-3, and of the $\boldsymbol{S}_3$ group in Table 5-2. The character table of the $\boldsymbol{S}_5$ group is given in Table 9-1. We label the irreducible representations according to the conventions used for MS groups. The reader can determine the $r_{\max}$ for each partition in Eq. (9-87) (by determining how many standard tableau there are for each partition) and test if they give the dimensions of the irreducible representations of $\boldsymbol{S}_5$. The irreducible representations Γ_1 and Γ_2 are the dual of each other in $\boldsymbol{S}_5$ (where $\Gamma = A$, G or H); for example, an orbital wavefunction of G_1 symmetry is allowed by the Pauli exclusion principle to combine with a spin function of G_2 symmetry to give a spin-orbital of $\Gamma^{(e)}(\mathrm{A}) = A_2$ symmetry.

Table 9-1

The character table of the group $\boldsymbol{S}_5$

	E	(12)	(12)(34)	(123)	(12)(345)	(1234)	(12345)
	1	10	15	20	20	30	24
A_1 :	1	1	1	1	1	1	1
A_2 :	1	−1	1	1	−1	−1	1
G_1 :	4	2	0	1	−1	0	−1
G_2 :	4	−2	0	1	1	0	−1
H_1 :	5	1	1	−1	1	−1	0
H_2 :	5	−1	1	−1	−1	1	0
I :	6	0	−2	0	0	0	1

[a] One representative element in each class is given, and the number written below each element is the number of elements in the class.

Closely related to the symmetric group approach, but conceptually very different, is the *unitary group approach*. In general, both approaches are designed to handle the spin symmetry of the problem, as well as to provide efficient ways of performing the required computations, but computer programs based on these two approaches are entirely different. The unitary group $\boldsymbol{U}(n)$ consists of all unitary transformations that lead from one orthonormal basis in n orbitals to another, and it uses Weyl tableau rather than Young tableau. The unitary group approach is good not only for CI but for any formalism based on using spin-adapted functions, and recently it has been developed for coupled cluster (CCSD) calculations. The book by Pauncz (1995) discusses the unitary group approach as well as the symmetric group approach.

9.5 SUMMARY

In order that we can solve the rovibronic Schrödinger equation for a molecule it is usually a practical necessity that we make the Born-Oppenheimer approximation. In this approximation we start by solving, in an *ab initio* calculation, the Schrödinger equation for the electrons of the molecule moving relative to fixed nuclei. The *ab initio* calculation must, at least in principle, be carried out for all possible nuclear geometries. It yields the electronic wavefunction and the Born-Oppenheimer potential energy function for each electronic state. Very frequently *ab initio* calculations are made by means of the *SCF-CI* method, which we have outlined in the present chapter, and the form obtained for the electronic wavefunction in this case is given in Eq. (9-83). We denote the electronic wavefunction as $\Phi_{\text{elec}}^{(e,S,m_S)}$, and we show how it is classified by symmetry in Chapter 12. The Born-Oppenheimer potential energy function V_{N} [see Eq. (9-61)] is used in the rotation-vibration Hamiltonian, and this is the subject of the next chapter.

BIBLIOGRAPHICAL NOTES

The Born-Oppenheimer approximation

The classic references are the following:
Born and Oppenheimer (1927).
Born (1951).
Born and Huang (1956).

An introductory account is given in Chapter 11 of Pilar (1990).

Ab initio theory

Some introductory textbooks:

Pilar (1990).
Szabo and Ostlund (1982).
Hehre, Radom, Schleyer, and Pople (1986).
Hinchcliffe (1988).

Some more advanced discussions:

Methods in Computational Molecular Physics (1992).
Clementi and Corongiu (1995).
Bürger and Thiel (1997). This paper discusses how *ab initio* calculations can be used to assist the spectroscopic detection and characterization of reactive molecules.

10

The Coordinates and Momenta in the Rotation-Vibration Hamiltonian

The coordinates used in the rotation-vibration Schrödinger equation are introduced for nonlinear rigid molecules. The coordinates are chosen in an attempt to minimize the terms that spoil the separation of the equation into a rotational and (3N−6) vibrational parts. We use the Eckart conditions to define the (x, y, z) molecule fixed axes (and hence the rovibronic angular momentum operator components $\hat{J}_\alpha$, where $\alpha = xyz$), and the l-matrix to define the normal coordinates Q_r (and conjugate momenta $\hat{P}_r$). The rotation-vibration Hamiltonian expressed in terms of J_α, Q_r, and $\hat{P}_r$ is presented. We do not repeat the derivation of the rotation-vibration Hamiltonian given in Wilson, Decius and Cross (1955) and other places. Our aim is to complement that work by explaining the importance of the choice of the coordinates and momenta.

10.1 INTRODUCTION

After making the Born-Oppenheimer approximation [see Eqs. (9-48)-(9-61)] we obtain the following Schrödinger equation for the rotation-vibration motion:

$$(\hat{T}_{\mathrm{N}} + V_{\mathrm{N}} - E_{\mathrm{rv}})\Phi_{\mathrm{rv}}(\xi_2, \eta_2, \zeta_2, \ldots, \zeta_N) = 0, \tag{10-1}$$

where

$$T_{\mathrm{N}} = -\frac{\hbar^2}{2}\sum_{i=2}^{N}\frac{\nabla_i^2}{m_i} + \frac{\hbar^2}{2M_{\mathrm{N}}}\sum_{i,j=2}^{N}\nabla_i \cdot \nabla_j, \tag{10-2}$$

$$\nabla_i^2 = \frac{\partial^2}{\partial\xi_i^2} + \frac{\partial^2}{\partial\eta_i^2} + \frac{\partial^2}{\partial\zeta_i^2}, \tag{10-3}$$

$$\nabla_i \cdot \nabla_j = \frac{\partial^2}{\partial\xi_i\partial\xi_j} + \frac{\partial^2}{\partial\eta_i\partial\eta_j} + \frac{\partial^2}{\partial\zeta_i\zeta_j}. \tag{10-4}$$

and V_N is the internuclear potential energy function obtained after solving the electronic Schrödinger equation [see Eqs. (9-55) and (9-61)]. The (ξ, η, ζ) axis system has origin at the nuclear center of mass and is parallel to the space fixed axis system.

To introduce rotational and vibrational coordinates it is necessary to introduce a set of (x, y, z) axes with origin at the nuclear center of mass and with an orientation relative to the (ξ, η, ζ) axes defined by the positions of the nuclei. These axes should be called 'nuclear fixed' but they have come to be called 'molecule fixed' axes; their orientation is determined by the coordinates of the nuclei only, and the coordinates of the electrons are not involved. The (x, y, z) and (ξ, η, ζ) axis systems are always chosen to be right handed. For any placement of the N nuclei in space [i.e., any set of values for the $(3N-3)$ independent coordinates ξ_i, η_i and ζ_i of the nuclei] there is an unambiguous way of specifying the orientation of the (x, y, z) axes with respect to the (ξ, η, ζ) axes. Three equations are required to define the three Euler angles that specify this orientation, and the equations used are the Eckart equations [Eckart (1935)]. As we will see the rotational basis wavefunctions will be functions of the Euler angles. In general the Eckart equations optimize the separation of the rotational and vibrational degrees of freedom in the rotation-vibration Schrödinger equation. The $(3N-6)$ independent coordinates $x_i - x_i^e$, $y_i - y_i^e$, and $z_i - z_i^e$ that are obtained once the (x, y, z) axes have been defined are used to construct the vibrational normal coordinates [where x_i^e, y_i^e, and z_i^e are the values of the coordinates at equilibrium]. We must first define the Euler angles.

10.1.1 The Euler angles

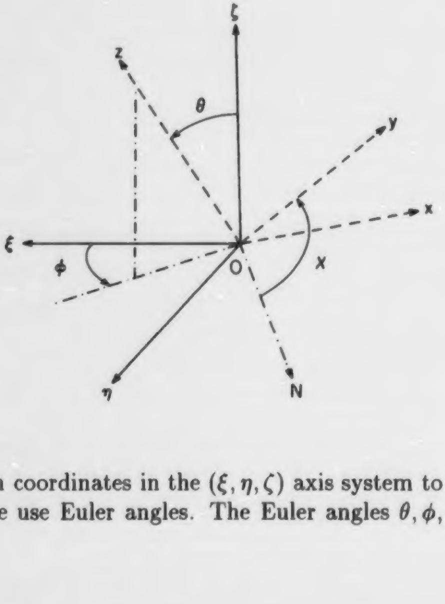


Fig. 10-1. The definition of the Euler angles (θ, ϕ, χ) that relate the orientation of the molecule fixed (x, y, z) axes to the (ξ, η, ζ) axes. The origin of both axis systems is at the nuclear center of mass O, and the node line ON is directed so that a right handed screw is driven along ON in its positive direction by twisting it from ζ to z through θ where $0 \leq \theta \leq \pi$. ϕ and χ have the ranges 0 to 2π. χ is measured from the node line.

To relate the nuclear and electron coordinates in the (ξ, η, ζ) axis system to those in the (x, y, z) axis system we use Euler angles. The Euler angles θ, ϕ, and χ are defined in Fig. 10-1 and we follow the convention used in Wilson, Decius, and Cross (1955). We use θ, ϕ, and χ to define the orientation of the (x, y, z) axis system relative to the (ξ, η, ζ) axis system in the same way that β, α, and γ are used in Fig. 7-1 to relate the orientation of one space fixed axis system (X', Y', Z') to another space fixed axis system (X, Y, Z). The Euler angles are restricted to the ranges $0 \leq \theta \leq \pi, 0 \leq \phi \leq 2\pi, 0 \leq \chi \leq 2\pi$. For any particle in the molecule (nucleus or electron) we can relate its coordinates in the (ξ, η, ζ) and (x, y, z) axis systems by writing

$$\begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} = \begin{bmatrix} \lambda_{x\xi} & \lambda_{x\eta} & \lambda_{x\zeta} \\ \lambda_{y\xi} & \lambda_{y\eta} & \lambda_{y\zeta} \\ \lambda_{z\xi} & \lambda_{z\eta} & \lambda_{z\zeta} \end{bmatrix} \begin{bmatrix} \xi_i \\ \eta_i \\ \zeta_i \end{bmatrix}, \tag{10-5}$$

where

$$\lambda_{x\xi} = \cos(x\mathrm{O}\xi), \qquad \text{etc.}, \tag{10-6}$$

and these are elements of the direction cosine matrix. The direction cosines can be expressed in terms of the Euler angles as follows [see Table I-1 in Wilson, Decius, and Cross (1955)]:

$$\begin{aligned} \lambda_{x\xi} &= \cos\theta\cos\phi\cos\chi - \sin\phi\sin\chi, & \lambda_{x\eta} &= \cos\theta\sin\phi\cos\chi + \cos\phi\sin\chi, \\ \lambda_{y\xi} &= -\cos\theta\cos\phi\sin\chi - \sin\phi\cos\chi, & \lambda_{y\eta} &= -\cos\theta\sin\phi\sin\chi + \cos\phi\cos\chi, \\ \lambda_{z\xi} &= \sin\theta\cos\phi, & \lambda_{z\eta} &= \sin\theta\sin\phi, \end{aligned}$$

$$\begin{aligned} \lambda_{x\zeta} &= -\sin\theta\cos\chi, \\ \lambda_{y\zeta} &= \sin\theta\sin\chi, \\ \lambda_{z\zeta} &= \cos\theta. \end{aligned} \tag{10-7}$$

10.1.2 Axis systems

Notice that we have now introduced four Cartesian axis systems:

(a) An (X, Y, Z) axis system fixed in space. This is the space fixed axis system, and it is used to set up the Hamiltonian initially as the sum of $\hat{T}$ in Eq. (7-2) and V in Eq. (7-19).

(b) An (X, Y, Z) axis system parallel to the (X, Y, Z) axis system and with its origin at the molecular center of mass. The molecular center of mass has coordinates (X_0, Y_0, Z_0) in the (X, Y, Z) axis system. This axis system is introduced to facilitate the separation of translation, and after making this separation the internal dynamics Hamiltonian $\hat{H}_{\mathrm{int}}$ is given by the expression in Eq. (7-28).

(c) An (ξ, η, ζ) axis system parallel to the (X, Y, Z) and (X, Y, Z) axis systems and with its origin at the nuclear center of mass. The nuclear center of mass has coordinates $(X_{\mathrm{NCM}}, Y_{\mathrm{NCM}}, Z_{\mathrm{NCM}})$ in the (X, Y, Z) axis system.

This axis system is introduced to facilitate the separation of the electronic and nuclear coordinates in the rovibronic Hamiltonian of Eq. (7-29). The rovibronic Schrödinger equation obtained is given in Eq. (9-48). After making the Born-Oppenheimer approximation the rotation-vibration Schrödinger equation in this coordinate system is as given in Eq. (10-1).

(d) An (x, y, z) axis system with its origin at the nuclear center of mass [as for the (ξ, η, ζ) axis system] and with orientation in the (ξ, η, ζ) system defined by the nuclear coordinates; the orientation is specified by the values of the Euler angles (θ, ϕ, χ). This is the molecule fixed axis system, and it is introduced to optimize the separation of the Schrödinger equation of Eq. (10-1) into rotational and vibrational parts with minimal approximation.

10.1.3 Changing to rovibrational coordinates

We have to change coordinates in the Schrödinger equation of Eq. (10-1) from $(\xi_2, \eta_2, \zeta_2, \ldots, \xi_N, \eta_N, \zeta_N)$ to the rotation-vibration coordinates $(\theta, \phi, \chi, Q_1, \ldots, Q_{3N-6})$, where the Q_r (the vibrational normal coordinates) are linear combinations of the nuclear displacement coordinates $\Delta x_i = x_i - x_i^e$, $\Delta y_i = y_i - y_i^e$, and $\Delta z_i = z_i - z_i^e$.

To begin with it is instructive to look at the effect of this coordinate change on the electronic kinetic energy operator T_e; since the Euler angles are independent of the (ξ, η, ζ) coordinates of the electrons we can make the coordinate change easily. The electronic kinetic energy operator in the (ξ, η, ζ) axis system is given by [see Eq. (9-49)]

$$T_e = -\frac{\hbar^2}{2m_e} \sum_{i=N+1}^{l} \nabla_i^2 - \frac{\hbar^2}{2M_N} \sum_{i,j=N+1}^{l} \nabla_i \cdot \nabla_j. \tag{10-8}$$

Using Eq. (10-5) for an electron we have the simple results that

$$\frac{\partial x_k}{\partial \xi_j} = \delta_{kj} \lambda_{x\xi} \tag{10-9}$$

and

$$\frac{\partial^2 x_k}{\partial \xi_j^2} = 0, \tag{10-10}$$

where $k, j = N+1, \ldots, l$, with similar equations for the derivatives involving y, z, η, and ζ. Using the chain rule [Eqs. (7-8) and (7-9)], and the fact that the direction cosine matrix is orthonormal, we can easily derive that

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}, \tag{10-11}$$

and

$$\nabla_i \cdot \nabla_j = \frac{\partial^2}{\partial x_i \partial x_j} + \frac{\partial^2}{\partial y_i \partial y_j} + \frac{\partial^2}{\partial z_i \partial z_j}. \tag{10-12}$$

We see that in the molecule fixed (x, y, z) axis system the electronic kinetic energy operator T_e for any molecule is given by Eq. (10-8) with substitutions from Eqs. (10-11) and (10-12). A rotation of the axis system in a manner defined purely by the nuclear coordinates has not changed the form of T_e and the use of the Method I coordinate transformation is very simple.

Let us attempt to follow the same procedure (Method I) for the nuclear kinetic energy operator T_N. From Eq. (10-5) for the nuclear coordinates we have

$$\frac{\partial x_k}{\partial \xi_j} = \delta_{kj}\lambda_{x\xi} + \frac{\partial \lambda_{x\xi}}{\partial \xi_j}\xi_k + \frac{\partial \lambda_{x\eta}}{\partial \xi_j}\eta_k + \frac{\partial \lambda_{x\zeta}}{\partial \xi_j}\zeta_k \tag{10-13}$$

$$= \delta_{kj}\lambda_{x\xi} + (xk), \tag{10-14}$$

where $j = 2, \ldots, N$ and $k = 2, \ldots, l$; we have introduced (xk) as an abbreviation for the last three terms in Eq. (10-13). Similar expressions for $(\partial y_k/\partial \xi_j)$ and $(\partial z_k/\partial \xi_j)$ will involve (yk) and (zk) terms. Using Eq. (7-8) we can write (for a nucleus j)

$$\frac{\partial}{\partial \xi_j} = \sum_{k=2}^{l}\left[\left(\frac{\partial x_k}{\partial \xi_j}\right)\frac{\partial}{\partial x_k} + \left(\frac{\partial y_k}{\partial \xi_j}\right)\frac{\partial}{\partial y_k} + \left(\frac{\partial z_k}{\partial \xi_j}\right)\frac{\partial}{\partial z_k}\right] \tag{10-15}$$

$$= \lambda_{x\xi}\frac{\partial}{\partial x_j} + \lambda_{y\xi}\frac{\partial}{\partial y_j} + \lambda_{z\xi}\frac{\partial}{\partial z_j} + \sum_{k=2}^{l}\left[(xk)\frac{\partial}{\partial x_k} + (yk)\frac{\partial}{\partial y_k} + (zk)\frac{\partial}{\partial z_k}\right]. \tag{10-16}$$

Without writing the second derivatives it is clear that the terms involving (xk), (yk), and (zk) result in derivatives with respect to the electron coordinates being introduced into the expression for T_N. Hence although by using (ξ, η, ζ) coordinates we achieve a complete separation of the electronic and nuclear coordinates in the kinetic energy operator $(T_e + T_N)$ when we change to (x, y, z) coordinates (in order to separate the rotational and vibrational coordinates) we introduce the electronic coordinates back into T_N. The effect of the nuclear-electronic coupling terms introduced into T_N is, however, generally small and a price well worth paying for the simplification in the rotation-vibration Hamiltonian that is obtained by using the (x, y, z) coordinates. From the mathematics of the coordinate change we see that the derivatives with respect to electron coordinates occur in T_N because the (x, y, z) coordinates of the electrons depend on the (ξ, η, ζ) coordinates of the nuclei through the dependence of the direction cosine matrix elements on the nuclear coordinates. Physically we are now referring the electrons to the (x, y, z) axis system which rotates with the nuclei, and the electrons are subject to Coriolis forces in this axis system; this makes itself felt by the resultant introduction of terms into T_N coupling the electronic angular momentum with the rovibronic angular momentum [the terms involving the electron derivatives in T_N eventually reduce to this]. It is possible to derive the rovibrational Schrödinger equation using a Method I coordinate change approach [see, for example, Louck (1976)] but traditionally a Method II approach is used.

A Method II derivation of $T_{\rm N}$ in the rotation-vibration coordinates begins with the following expression for the classical nuclear kinetic energy:

$$T_{\rm N} = \frac{1}{2}\sum_{i=1}^{N} m_i(\dot{\xi}_i{}^2 + \dot{\eta}_i{}^2 + \dot{\zeta}_i{}^2), \tag{10-17}$$

where we have the restrictions

$$\sum_{i=1}^{N} m_i\xi_i = \sum_{i=1}^{N} m_i\eta_i = \sum_{i=1}^{N} m_i\zeta_i = 0, \tag{10-18}$$

since the (ξ, η, ζ) axis system has origin at the nuclear center of mass. This classical expression for $T_{\rm N}$ leads to the quantum mechanical expression $\hat{T}_{\rm N}$ given in Eq. (10-2); see Eqs. (7-2)-(7-18). The Method II derivation of the quantum mechanical expression for $T_{\rm N}$ involves use of the Podolsky trick after having changed to the rotation-vibration coordinates in the classical expression for $T_{\rm N}$. The details are given in Chapter 11 of Wilson, Decius, and Cross (1955). A simplification of this kinetic energy operator was discovered by Watson (1968). We will not duplicate this derivation or simplification here. To determine the effect of symmetry operations on the rotation-vibration wavefunctions we must, however, understand the coordinates and these will be discussed. The two central parts of the coordinate change to the rotation-vibration coordinates are (a) the Eckart equations [Eckart (1935)] which define the Euler angles, and (b) the l matrix [see, for example, Nielsen (1959)] which defines the normal coordinates.

10.2 THE ECKART EQUATIONS

The Eckart equations enable us to determine the Euler angles [i.e., the orientation of the molecule fixed (x, y, z) axes] from the values of the coordinates of the nuclei $(\xi_2, \eta_2, \zeta_2, \dots, \xi_N, \eta_N, \zeta_N)$. To determine the Euler angles from the nuclear coordinates we need three equations which we might write as

$$\theta = f_\theta(\xi_2, \dots, \zeta_N), \tag{10-19}$$

$$\phi = f_\phi(\xi_2, \dots, \zeta_N), \tag{10-20}$$

and

$$\chi = f_\chi(\xi_2, \dots, \zeta_N). \tag{10-21}$$

Having oriented the (x, y, z) axes in the molecule by using the equations represented above we can determine the (x, y, z) coordinates of each nucleus in the molecule. Such a calculation could be made when the nuclei are in their equilibrium configuration and we would obtain the *equilibrium nuclear coordinates* (x_i^e, y_i^e, z_i^e) for each nucleus i. For a given distorted nuclear configuration the displacements $\Delta x_i = (x_i - x_i^e)$, $\Delta y_i = (y_i - y_i^e)$, and $\Delta z_i = (z_i - z_i^e)$ would be the vibrational displacement coordinates.

We would like to choose f_θ, f_ϕ and f_χ in Eqs. (10-19)-(10-21) so that if we were to express the nuclear kinetic energy in terms of the Euler angles and vibrational displacements there would be a complete separation into a rotational part (involving only the Euler angles) and a vibrational part (involving only the vibrational displacement coordinates). To do this we would have to eliminate the vibrational angular momentum $\boldsymbol{J}_{\text{vib}}$ in the (x, y, z) axis system; if $\boldsymbol{J}_{\text{vib}}$ were nonvanishing there would be a Coriolis coupling of it to the rovibronic angular momentum $\boldsymbol{J}$ which would spoil the separation of variables. The vibrational angular momentum is given by

$$\boldsymbol{J}_{\text{vib}} = \sum_i m_i \boldsymbol{r}_i \times \dot{\boldsymbol{r}}_i, \tag{10-22}$$

where m_i is the mass of the ith nucleus, $\boldsymbol{r}_i$ has components (x_i, y_i, z_i) and the velocity $\dot{\boldsymbol{r}}_i$ has components $(\dot{x}_i, \dot{y}_i, \dot{z}_i)$ in the (x, y, z) axis system. If f_θ, f_ϕ and f_χ could be chosen so that the $\boldsymbol{r}_i$ and $\dot{\boldsymbol{r}}_i$ satisfy

$$\sum_i m_i \boldsymbol{r}_i \times \dot{\boldsymbol{r}}_i = 0, \tag{10-23}$$

then there would be no vibrational angular momentum in the (x, y, z) axis system and no Coriolis coupling terms to spoil the separation of rotation from vibration.

Unfortunately, with only three equations [Eqs. (10-19)-(10-21)] at our disposal we cannot define θ, ϕ, and χ so that the resultant (x_i, y_i, z_i) *and* $(\dot{x}_i, \dot{y}_i, \dot{z}_i)$ satisfy Eq. (10-23). However, for a rigid molecule the nuclei do not depart far from the nuclear equilibrium configuration and to a good approximation we have

$$\boldsymbol{J}_{\text{vib}} \approx \sum_i m_i \boldsymbol{r}_i{}^e \times \dot{\boldsymbol{r}}_i, \tag{10-24}$$

where $\boldsymbol{r}_i{}^e$ has components $(x_i{}^e, y_i{}^e, z_i{}^e)$. We can choose f_θ, f_ϕ, and f_χ so that the $\dot{x}_i$, $\dot{y}_i$, and $\dot{z}_i$ satisfy

$$\sum_i m_i \boldsymbol{r}_i{}^e \times \dot{\boldsymbol{r}}_i = 0, \tag{10-25}$$

and in the (x, y, z) axis system so defined $\boldsymbol{J}_{\text{vib}}$ and the Coriolis coupling will be small. Equation (10-25) follows by differentiating with respect to time of the *Eckart equation*, which is

$$\sum_i m_i \boldsymbol{r}_i{}^e \times \boldsymbol{r}_i = 0. \tag{10-26}$$

The three components of this equation are

$$\sum_i m_i(x_i{}^e y_i - y_i{}^e x_i) = 0, \tag{10-27}$$

$$\sum_i m_i(y_i{}^e z_i - z_i{}^e y_i) = 0, \tag{10-28}$$

and

$$\sum_i m_i(z_i{}^e x_i - x_i{}^e z_i) = 0. \tag{10-29}$$

Choosing the orientation of the (x, y, z) axes so that Eqs. (10-27)-(10-29) are satisfied results in Eq. (10-25) being satisfied so that $\boldsymbol{J}_{\text{vib}}$ is small. The origin of the (x, y, z) axis system is the nuclear center of mass so the nuclear coordinates must also satisfy

$$\sum_i m_i \boldsymbol{r}_i{}^e = \sum_i m_i \boldsymbol{r}_i = 0. \tag{10-30}$$

For the equilibrium nuclear configuration we choose the orientation of the (x, y, z) axes so that they are the principal axes of inertia in order to simplify the rotational kinetic energy. The *inertia matrix* $\boldsymbol{I}$ has the diagonal elements

$$I_{\alpha\alpha} = \sum_i m_i\ (\beta_i^2 + \gamma_i^2) \tag{10-31}$$

(called *moments of inertia*), where $\alpha\beta\gamma$ is a permutation of xyz, and the off-diagonal elements

$$I_{\alpha\beta} = -\sum_i m_i \alpha_i \beta_i \tag{10-32}$$

(the $\sum_i m_i \alpha_i \beta_i$ are called[1] *products of inertia*), where $\alpha \neq \beta$. Using principal inertial axes the off-diagonal elements $I_{\alpha\beta}$ vanish. Thus the (x, y, z) axes are located in the equilibrium nuclear configuration so that

$$\sum_i m_i x_i{}^e y_i{}^e = \sum_i m_i y_i{}^e z_i{}^e = \sum_i m_i z_i{}^e x_i{}^e = 0. \tag{10-33}$$

To use the Eckart equations [Eqs. (10-27)-(10-29)] in order to determine the Euler angles θ, ϕ, and χ from the nuclear coordinates $(\xi_2, \ldots, \zeta_N)$ we proceed as follows. Expressing the (x_i, y_i, z_i) coordinates in terms of the (ξ_i, η_i, ζ_i) coordinates by using the direction cosine matrix elements $\lambda_{\alpha\tau}$ [where $\alpha = x, y$, or z and $\tau = \xi, \eta$, or ζ; see Eq. (10-6)] we can write the three Eckart equations as

$$[x\xi]\lambda_{y\xi} + [x\eta]\lambda_{y\eta} + [x\zeta]\lambda_{y\zeta} - [y\xi]\lambda_{x\xi} - [y\eta]\lambda_{x\eta} - [y\zeta]\lambda_{x\zeta} = 0, \tag{10-34}$$

$$[y\xi]\lambda_{z\xi} + [y\eta]\lambda_{z\eta} + [y\zeta]\lambda_{z\zeta} - [z\xi]\lambda_{y\xi} - [z\eta]\lambda_{y\eta} - [z\zeta]\lambda_{y\zeta} = 0, \tag{10-35}$$

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[1] Note that in Eq. 8 of Section 11-1 of Wilson, Decius and Cross (1955) the products of inertia are denoted $I_{\alpha\beta}$.

and

$$[z\xi]\lambda_{x\xi} + [z\eta]\lambda_{x\eta} + [z\zeta]\lambda_{x\zeta} - [x\xi]\lambda_{z\xi} - [x\eta]\lambda_{z\eta} - [x\zeta]\lambda_{z\zeta} = 0, \tag{10-36}$$

where

$$[\alpha\tau] = \sum_{i=1}^{N} m_i \alpha_i{}^{e} \tau_i, \tag{10-37}$$

with $\alpha = x, y,$ or z and $\tau = \xi, \eta,$ or ζ. Knowing the equilibrium coordinates of the nuclei in the (x, y, z) axis system [having initially used Eq. (10-33) to determine $x_i{}^{e}$, $y_i{}^{e}$, and $z_i{}^{e}$] we can use the values of the (ξ_i, η_i, ζ_i) coordinates to determine the values of the $[\alpha\tau]$. We can then set up the three transcendental equations, Eqs. (10-34)-(10-36), in the Euler angles using Eq. (10-7). Solving these equations simultaneously gives the values of the Euler angles as we show in a numerical example in the next section. The Eckart equations lead to these three simultaneous transcendental equations in the Euler angles and not to three simple equations as suggested by Eqs. (10-19)-(10-21).

10.2.1 A numerical example involving the Eckart equations

We will use a numerical example involving the water molecule to demonstrate the coordinate change $(\xi_2, \ldots, \zeta_N)$ to $(\theta, \phi, \chi, \Delta\alpha_i)$, and to show the central place of the Eckart equations in this coordinate change.

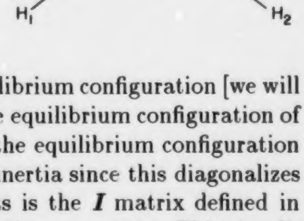

Fig. 10-2. A water molecule in its equilibrium configuration with molecule fixed (x, y, z) axes attached. The oxygen nucleus is labeled 3.

In Fig. 10-2 we show a water molecule in its equilibrium configuration [we will take $r(\mathrm{OH}) = 0.957$Å and $\angle\,(\mathrm{HOH}) = 105°$ for the equilibrium configuration of the water molecule]. The molecule fixed axes of the equilibrium configuration of a molecule are located as the principal axes of inertia since this diagonalizes $\boldsymbol{\mu}^{e} = (\boldsymbol{I}^{e})^{-1}$, where $\boldsymbol{I}^{e}$ has the diagonal elements is the $\boldsymbol{I}$ matrix defined in Eqs. (10-31) and (10-32), calculated at the equilibrium geometry. This simplifies the rotational kinetic energy as we shall see below. Since each of the three $x, y,$ and z axes can be identified with any of the three principal axes and the signs of any of the $x, y,$ and z axes can be reversed all without introducing off-diagonal elements into $\boldsymbol{\mu}^{e}$ we have many possible ways of locating the (x, y, z) axes as principal axes. The three principal axes of a molecule are by convention labeled a, b, and c in such a manner that the moments of inertia about the axes are in the order $I_{aa} < I_{bb} < I_{cc}$. We can identify the z axis with any of the three principal axes and depending on whether it is identified with the a, b, or c axis we name the convention adopted as type I, II, or III. We add a superscript r or l depending on whether a right or left handed (x, y, z) axis system is used. For the water molecule we adopt a I^r convention (see Fig. 10-2) in which the z axis is located so that H_2 has a positive z coordinate, the x axis is located so that the oxygen nucleus has a positive x coordinate, and the y axis is located so that the axis system is right handed. Using 1 u and 16 u as the hydrogen and oxygen nuclear masses we determine that (in Å)

$$\begin{aligned} &x_1{}^{\mathrm{e}} = x_2{}^{\mathrm{e}} = -0.5178, \qquad x_3{}^{\mathrm{e}} = 0.06473, \\ &y_1{}^{\mathrm{e}} = y_2{}^{\mathrm{e}} = y_3{}^{\mathrm{e}} = 0, \\ &z_1{}^{\mathrm{e}} = -z_2{}^{\mathrm{e}} = -0.7592, \qquad z_3{}^{\mathrm{e}} = 0, \end{aligned} \tag{10-38}$$

where we label the oxygen nucleus 3.

As a water molecule moves in space in its equilibrium configuration it is always easy [using the results in Eq. (10-38)] to determine the orientation of the (x, y, z) axes and hence the Euler angles. For example, suppose that the (X_i, Y_i, Z_i) coordinates of the nuclei in the space fixed (X, Y, Z) axis system are (in Å)

$$(0.3733, -0.3626, -0.8031), \quad (0.7529, 0.2949, 0.5118), \quad (0, 0, 0) \tag{10-39}$$

for nuclei H_1, H_2, and O_3, respectively. Moving to the (ξ, η, ζ) axis system with origin at the nuclear center of mass [which we determine to have coordinates $(0.0626, -0.00376, -0.0162)$ in the (X, Y, Z) axis system] we find the (ξ_i, η_i, ζ_i) coordinates to be (in Å)

$$\begin{aligned} &(0.3107, -0.3588, -0.7869), (0.6903, 0.2987, 0.5280), \\ &\qquad \text{and} \quad (-0.0626, 0.00376, 0.0162). \end{aligned} \tag{10-40}$$

Knowing the equilibrium nuclear coordinates in the (x, y, z) axis system [from Eq. (10-38)] we can determine the Euler angles by using the direction cosine matrix elements [Eq. (10-7)] as follows.

To determine θ we use the fact that all $y_i{}^{\mathrm{e}} = 0$ and from Eq. (10-7) we obtain

$$\zeta_i = x_i^{\mathrm{e}}(-\sin\theta\cos\chi) + z_i^{\mathrm{e}}\cos\theta, \tag{10-41}$$

from which, since $x_1{}^{\mathrm{e}} = x_2{}^{\mathrm{e}}$, we obtain

$$(\zeta_2 - \zeta_1) = (z_2{}^{\mathrm{e}} - z_1{}^{\mathrm{e}})\cos\theta, \tag{10-42}$$

and thus

$$\theta = \arccos[(\zeta_2 - \zeta_1)/(z_2{}^{\mathrm{e}} - z_1{}^{\mathrm{e}})]. \tag{10-43}$$

Since $0 \leq \theta \leq \pi$ we can unambiguously determine θ from Eq. (10-43) by substituting in the appropriate values for z_i^{e} and ζ_i from Eqs. (10-38) and (10-40); we obtain

$$\theta = 30^\circ. \tag{10-44}$$

To determine ϕ we use equations similar to Eq. (10-42) for ξ_i and η_i, together with Eq. (10-43) for θ, to derive that

$$\phi = \arccos\{(\xi_2 - \xi_1)/[(z_2^{\mathrm{e}} - z_i^{\mathrm{e}})^2 - (\zeta_2 - \zeta_1)^2]^{1/2}\} \tag{10-45}$$

and

$$\phi = \arcsin\{(\eta_2 - \eta_1)/[(z_2^{\mathrm{e}} - z_1^{\mathrm{e}})^2 - (\zeta_2 - \zeta_1)^2]^{1/2}\}. \tag{10-46}$$

Since $0 \leq \phi \leq 2\pi$ we need both these equations for an unambiguous determination of ϕ. From these equations we determine

$$\phi = 60^\circ. \tag{10-47}$$

For the angle χ we obtain

$$\chi = \arccos\{-\zeta_3(z_2^{\mathrm{e}} - z_1^{\mathrm{e}})[(z_2^{\mathrm{e}} - z_1^{\mathrm{e}})^2 - (\zeta_2 - \zeta_1)^2]^{-1/2}/x_3^{\mathrm{e}}\} \tag{10-48}$$

and to make an unambiguous determination ($0 \leq \chi \leq 2\pi$) we also use

$$\cos\theta\cos\phi\cos\chi - \sin\phi\sin\chi = (\xi_1 + \xi_2)/(x_1^{\mathrm{e}} + x_2^{\mathrm{e}}) \tag{10-49}$$

to give

$$\chi = 120^\circ. \tag{10-50}$$

A water molecule in its equilibrium configuration with this orientation is drawn in Fig. 10-3.

To determine the Euler angles of a molecule that is not in its equilibrium configuration we would proceed as in the preceding example if we defined the (x, y, z) axes as instantaneous principal axes. However for a deformed molecule it is better [as we have indicated in Eqs. (10-22)-(10-26)] to choose the (x, y, z) axes to be Eckart axes rather than principal axes. Principal axes are located so that the three equations $I_{xy} = I_{yz} = I_{zx} = 0$ are satisfied, whereas Eckart axes are located so that the three Eckart equations Eqs. (10-27)-(10-29) are satisfied. We see that we need to know the equilibrium (x, y, z) coordinates of the nuclei in order to be able to locate the Eckart axes when the molecule is not at equilibrium. We will use the water molecule as a numerical example of this.

We take a deformed water molecule having $r_{13} = 2.4193$ Å, $r_{23} = 0.9452$ Å, and $\angle$ (HOH) = 103.4°, and place it so that the (X, Y, Z) coordinates of the nuclei are

$$(0.9066, -0.9251, -2.0434), \quad (0.7690, 0.2778, 0.4742), \quad (0, 0, 0) \tag{10-51}$$

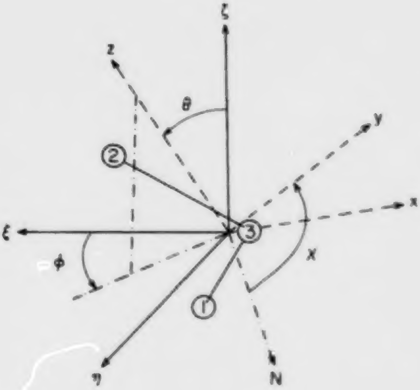

Fig. 10-3. A water molecule in its equilibrium configuration oriented with coordinates given by Eq. (10-40). The Euler angles (θ, ϕ, χ) are shown to be $(30°, 60°, 120°)$ in Eqs. (10-43)-(10-50).

for H_1, H_2, and O_3 respectively. The nuclear center of mass is determined to be located at $(0.0930, -0.0360, -0.0872)$ in the (X, Y, Z) axis system, so that the (ξ, η, ζ) coordinates of nuclei 1, 2, and 3 are, respectively

$$\begin{aligned}&(0.8136, -0.8891, -1.9562),\ (0.6760, 0.3138, 0.5614),\\ &\qquad \text{and} \quad (-0.0930, 0.0360, 0.0872). \end{aligned} \tag{10-52}$$

We now wish to use the Eckart equations and the equilibrium coordinates to determine the Euler angles of this deformed water molecule. The equilibrium coordinates are known and are given in Eq. (10-38). We use the form of the Eckart equations given in Eqs. (10-34)-(10-36) in this determination. The $[\alpha\tau]$ can be calculated from the $\alpha_i{}^e$ in Eq. (10-38) and from the τ_i in Eq. (10-52); the $\lambda_{\alpha\tau}$ are given in terms of the Euler angles in Eq. (10-7). Using these $[\alpha\tau]$ and $\lambda_{\alpha\tau}$ Eq. (10-34) becomes

$$\begin{aligned}&0.8676(\cos\theta\cos\phi\sin\chi + \sin\phi\cos\chi) + 0.3352(-\cos\theta\sin\phi\sin\chi + \cos\phi\cos\chi)\\ &\qquad + 0.8125(\sin\theta\sin\chi) = 0,\end{aligned} \tag{10-53}$$

Eq. (10-35) becomes

$$\begin{aligned}&-0.1045(\cos\theta\cos\phi\sin\chi + \sin\phi\cos\chi) - 0.9132(-\cos\theta\sin\phi\sin\chi\\ &\qquad + \cos\phi\cos\chi) - 1.9114(\sin\theta\sin\chi) = 0,\end{aligned} \tag{10-54}$$

and Eq. (10-36) becomes

$$\begin{aligned}&-0.1045(\cos\theta\cos\phi\cos\chi - \sin\phi\sin\chi) + 0.9132(\cos\theta\sin\phi\cos\chi + \cos\phi\sin\chi)\\ &\qquad - 1.9114\sin\theta\cos\chi + 0.8676\sin\theta\cos\phi - 0.3352\sin\theta\sin\phi\\ &\qquad - 0.8125\cos\theta = 0.\end{aligned} \tag{10-55}$$

These three simultaneous transcendental equations can be solved numerically using, for example, the Newton-Raphson method [see Margenau and Murphy

(1956), page 493], and one solution is

$$(\theta = 30^\circ, \phi = 60^\circ, \chi = 120^\circ). \tag{10-56}$$

This is depicted in Fig. 10-4. Other solutions, corresponding to other possible ways of locating a right handed (x, y, z) axis system as principal inertial axes on the equilibrium molecule, can also be obtained from the simultaneous solutions of Eqs. (10-53)-(10-55), but since the orientation of the axes must smoothly correlate with those of the equilibrium molecule as the distortion is removed we discard these alternate solutions. We will always discard such solutions in any later similar determinations, such as in the solution of Eq. (10-67) or in obtaining the result in Eq. (10-75). From the Euler angles we can determine the direction cosine matrix elements, and from these and the (ξ, η, ζ) coordinates of the nuclei we can determine the (x, y, z) coordinates of the nuclei [given in Eq. (10-68), which follows].

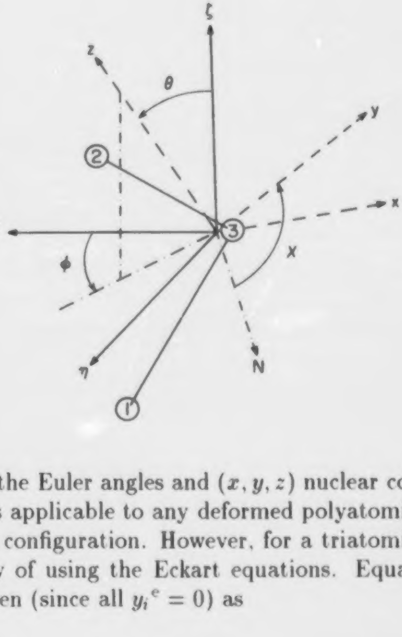

Fig. 10-4. A deformed water molecule with (ξ, η, ζ) coordinates given by Eq. (10-52). The Euler angles are shown to be $(30^\circ, 60^\circ, 120^\circ)$ in Eqs. (10-53)-(10-56); this results from using the Eckart equations.

The above method for determining the Euler angles and (x, y, z) nuclear coordinates from the Eckart equations is applicable to any deformed polyatomic molecule having a unique equilibrium configuration. However, for a triatomic molecule there is a rather simple way of using the Eckart equations. Equations (10-27) and (10-28) can be written (since all $y_i{}^{\mathrm{e}} = 0$) as

$$\sum_{i=1}^{3} m_i x_i^{\mathrm{e}} y_i = 0 \tag{10-57}$$

and

$$\sum_{i=1}^{3} m_i z_i^{\mathrm{e}} y_i = 0. \tag{10-58}$$

The center of mass condition Eq. (10-30) gives a third equation

$$\sum_{i=1}^{3} m_i y_i = 0. \tag{10-59}$$

These three equations lead directly to the result that

$$y_1 = y_2 = y_3 = 0. \tag{10-60}$$

Thus regardless of the extent of the deformation all three atoms lie in the xz plane of the molecule fixed axes if all $y_i^e = 0$. We use the third Eckart equation to determine the orientation of the x and z axes relative to the nuclear frame. To do this it is convenient to introduce the angle ε between the x axis direction and the line joining the nuclear center of mass to the oxygen nucleus as in Fig. 10-5. Using this angle, the cosine rule, and a fair amount of trigonometry we obtain

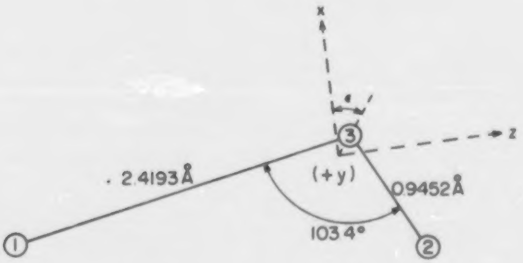

Fig. 10-5. The definition of the angle ε that shows how (x, y, z) axes are oriented on a deformed water molecule. The origin of the (x, y, z) axes is at the nuclear center of mass.

$$x_1 = 0.9330 \sin\varepsilon - 2.100 \cos\varepsilon, \tag{10-61}$$

$$z_1 = -0.9330 \cos\varepsilon - 2.100 \sin\varepsilon, \tag{10-62}$$

$$x_2 = -0.9330 \sin\varepsilon - 0.0203 \cos\varepsilon, \tag{10-63}$$

$$z_2 = 0.9330 \cos\varepsilon - 0.0203 \sin\varepsilon, \tag{10-64}$$

$$x_3 = 0.1325 \cos\varepsilon, \tag{10-65}$$

and

$$z_3 = 0.1325 \sin\varepsilon. \tag{10-66}$$

Substituting these values into Eq. (10-29), and using the equilibrium coordinates from Eq. (10-38), we obtain

$$-2.652 \sin\varepsilon + 1.579 \cos\varepsilon = 0, \tag{10-67}$$

from which we determine $\varepsilon = 30.77°$ and that the (x, y, z) nuclear coordinates are (in Å)

$$(-1.3270, 0, -1.8757), \quad (-0.4948, 0, 0.7911), \quad (0.1138, 0, 0.0678). \tag{10-68}$$

Relating these coordinates to the (ξ, η, ζ) coordinates of Eq. (10-52) we can determine the direction cosine matrix elements and thus the Euler angles [given in Eq. (10-56)].

Using the above (x, y, z) coordinates and subtracting the equilibrium coordinates [Eq. (10-38)] we determine the Cartesian displacement coordinates $(\Delta x_i, \Delta y_i, \Delta z_i)$ to be (in Å)

$$(-0.8092, 0, -1.1165), \quad (0.0230, 0, 0.0319), \quad (0.0491, 0, 0.0678). \tag{10-69}$$

It is instructive at this stage to imagine that we can pick up the equilibrium configuration water molecule, with its molecule fixed axes attached, from out of Fig. 10-2 and insert it into Fig. 10-4 in such a way that its (x, y, z) axes are coincident with those of the deformed molecule. In this composite figure the displacements of the nuclei of the deformed molecule away from those of the equilibrium molecule will be as given in Eq. (10-69). Figure 2-4 can be viewed as such a composite figure for ethylene. Writing $\alpha_i = \alpha_i{}^e + \Delta\alpha_i$ in Eqs. (10-27)-(10-29) we deduce three alternative Eckart equations:

$$\sum_{i=1}^{N} m_i(x_i{}^e \Delta y_i - y_i{}^e \Delta x_i) = 0, \tag{10-70}$$

$$\sum_{i=1}^{N} m_i(y_i{}^e \Delta z_i - z_i{}^e \Delta y_i) = 0, \tag{10-71}$$

and

$$\sum_{i=1}^{N} m_i(z_i{}^e \Delta x_i - x_i{}^e \Delta z_i) = 0. \tag{10-72}$$

The Cartesian displacement coordinates must satisfy these three equations (if we use Eckart axes) as well as the three center of mass equations [from Eq. (10-30)]

$$\sum_{i=1}^{N} m_i \Delta\alpha_i = 0, \tag{10-73}$$

where $\alpha = x, y$, or z.

Problem 10-1. Make the coordinate transformation from the (ξ, η, ζ) coordinates of Eq. (10-52) to $(\theta, \phi, \chi, \Delta\alpha_i)$ using molecule fixed (x, y, z) axes that are principal inertial axes rather than Eckart axes.

Answer. For a triatomic molecule one principal inertial axis is perpendicular to the plane of the three nuclei. To follow the axis labeling convention adopted for the molecule in its equilibrium configuration we must choose this axis to be the y axis; as a result $I_{xy} = I_{yz} = 0$. To determine the directions of the other principal axes we use the angle ε as introduced in Fig. 10-5, and the principal axis equation that defines ε is

$$\sum_{i=1}^{3} m_i x_i z_i = 0. \tag{10-74}$$

Substituting Eqs. (10-61)-(10-66) into this equation we determine that for principal axes

$$\varepsilon = 63.63^\circ. \tag{10-75}$$

Using this value ε in Eqs. (10-61)-(10-66) we determine the (x, y, z) coordinates of the three nuclei to be (in Å)

$$(-0.0967, 0, -2.296), \quad (-0.8448, 0, 0.3965), \quad (0.0588, 0, 0.1187). \tag{10-76}$$

Using the direction cosine matrix elements to relate these to the (ξ, η, ζ) coordinates we determine the Euler angles to be

$$(\theta, \phi, \chi) = (30.3^\circ, 128.3^\circ, 59.1^\circ). \tag{10-77}$$

The $(\Delta x_i, \Delta y_i, \Delta z_i)$ displacements from equilibrium are determined to be (in Å)

$$(0.4211, 0, -1.5368), \quad (-0.3270, 0, -0.3627), \quad (-0.0059, 0, 0.1187). \tag{10-78}$$

Comparing the solution to Problem 10-1 with the results in Eq. (10-56) we see that the Euler angles are changed drastically when we use principal axes rather than Eckart axes. In Fig. 10-6 the location of the Eckart axes and principal axes on this deformed water molecule are compared; in each case an equilibrium configuration water molecule having the same Euler angles, so that its (x, y, z) axes are coincident with those of the deformed molecule, is superimposed. We can appreciate from these figures that this deformation (a stretching of the $\mathrm{OH_1}$ bond) causes a significant rotation of principal axes (see Fig. 10-6b) but very little rotation of Eckart axes (see Fig. 10-6a). As we move $\mathrm{H_1}$ towards and away from $\mathrm{O_3}$ the Eckart axes will hardly move whereas the principal axes will twist back and forth about the y axis and much rotational motion is "mixed into" this vibrational motion. It can be shown that if we use principal axes the rotation-vibration mixing caused by the Coriolis coupling terms in the Hamiltonian is much larger than if we use Eckart axes; in fact the choice of Eckart axes generally minimizes these terms as discussed from Eq. (10-22) to Eq. (10-26). As a result, the separation of $\hat{T}_{\mathrm{N}}$ into rotational and vibrational parts is achieved with minimum approximation using the Eckart axes. This is why Eckart axes are used.

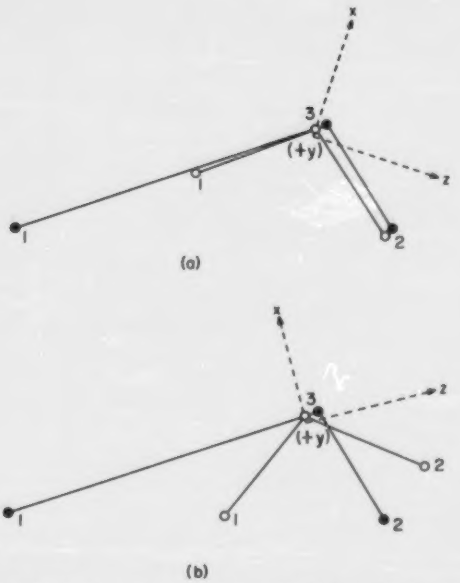

Fig. 10-6. (a) The deformed water molecule of Eq. (10-52) (shaded circles) with molecule fixed *Eckart axes* $(x, y; z)$ and an appropriately oriented water molecule in its equilibrium configuration (open circles). (b) The same with molecule fixed *principal axes* (x, y, z) and an appropriately oriented water molecule in its equilibrium configuration (open circles).

We can view the choice of axes in mathematical or physical terms. Mathematically we are changing the $(3N - 3)$ coordinates from $(\xi_2, \ldots, \zeta_N)$ to $(\theta, \phi, \chi, \Delta\alpha_i)$ where each of the coordinates $(\theta, \phi, \chi, \Delta\alpha_i)$ is a function of the coordinates $(\xi_2, \ldots, \zeta_N)$. We make this coordinate change in such a way that the rotation-vibration Hamiltonian can be separated with minimum approximation. The Eckart conditions generally ensure this. Physically we consider the (θ, ϕ, χ) coordinates to define the orientation of the molecule fixed axes, Our coordinate change then *defines* what we mean by "rotation." For example, if we stretch an OH bond in the water molecule it is obvious by how much the molecular center of mass has been translated (and therefore how much translational motion has occurred), but it is a matter of axis system definition as to how much we consider the molecule (or, equivalently, the molecule fixed axes) to have rotated. In our numerical example the deformation of a water molecule from the equilibrium configuration described by the (ξ, η, ζ) nuclear coordinates of Eq. (10-40) to those of Eq. (10-52) is *defined* as being a purely vibrational deformation using Eckart axes, since the Euler angles of the deformed configuration are the same as those of the equilibrium configuration. Using principal axes this is not the case.

In Figs. 4-5 to 4-7 each molecular figure shows a water molecule with the nuclei (solid circles) deformed away from equilibrium together with an equilibrium configuration water molecule and the molecule fixed (x, y, z) axes. To draw such a figure one starts from the deformed (instantaneous) water molecule and then determines how to locate the molecule fixed axes and equilibrium water molecule using the Eckart equations. Starting from the instantaneous (ξ, η, ζ) coordinates of the nuclei one uses the Eckart equations to determine the Euler angles. One can imagine that in each of these molecular figures a microscopic hand puts down the (x, y, z) axes, oriented with these Euler angles, to which an equilibrium water molecule is attached according to Fig. 10-2, on the instantaneous deformed water molecule.

10.3 ANGULAR MOMENTUM

One of the central themes of this chapter is the importance of choosing the right coordinates in which to express the Hamiltonian; we should say coordinates *and momenta*. After introducing the Euler angles the quantum mechanical Hamiltonian will involve the three momentum operators $\hat{P}_\theta = -i\hbar\partial/\partial\theta$, $\hat{P}_\phi = -i\hbar\partial/\partial\phi$, and $\hat{P}_\chi = -i\hbar\partial/\partial\chi$. It is very helpful to introduce three special linear combinations of these momentum operators which form the (x, y, z) components of the rovibronic (or rotational) angular momentum operator[2] $\hat{\boldsymbol{J}}$. The components of the angular momentum operator have properties that make determining basis wavefunctions and zero order eigenvalues of a Hamiltonian that involves them rather straightforward. In this section we will briefly summarize some of the properties of the angular momentum operators and eigenfunctions without giving proofs. A more complete discussion, with proofs, is given in Zare (1988) and in the references quoted there.

10.3.1 The rovibronic angular momentum operator

The rovibronic angular momentum operator $\hat{\boldsymbol{J}}$ in a molecule gives the angular momentum that arises from the orbital motion of the nuclei and electrons. From first principles, presuming there to be l particles (nuclei and electrons) in the molecule, the component of the rovibronic angular momentum operator relative to the space fixed ξ axis is given by

$$\hat{J}_\xi = -i\hbar \sum_{j=1}^{l} \left(\eta_j \frac{\partial}{\partial \zeta_j} - \zeta_j \frac{\partial}{\partial \eta_j} \right); \qquad (10\text{-}79)$$

$\hat{J}_\eta$ and $\hat{J}_\zeta$ are given by cyclic rearrangement. Expressing the (ξ, η, ζ) components in terms of $\hat{P}_\theta$, $\hat{P}_\phi$ and $\hat{P}_\chi$ we obtain

$$\hat{J}_\xi = -\sin\phi \hat{P}_\theta + \csc\theta \cos\phi \hat{P}_\chi - \cot\theta \cos\phi \hat{P}_\phi, \qquad (10\text{-}80)$$

$$\hat{J}_\eta = \cos\phi \hat{P}_\theta + \csc\theta \sin\phi \hat{P}_\chi - \cot\theta \sin\phi \hat{P}_\phi, \qquad (10\text{-}81)$$

---

[2] Remember that for the general case (i.e., non-singlet states) we should use $\hat{\boldsymbol{N}}$ for the rovibronic angular momentum operator (see footnote on page 138).

and

$$\hat{J}_\zeta = \hat{P}_\phi. \tag{10-82}$$

In the molecular Hamiltonian we need expressions for the components of the rovibronic angular momentum operator relative to the molecule fixed x, y and z axes, rather than to the space fixed axes, and one might think that equations analogous to Eq. (10-79), with ξ, η and ζ replaced by x, y and z, could be used to derive them. This is incorrect. As Van Vleck (1951) points out, the correct way to obtain the expressions for the molecule fixed components of the rovibronic angular momentum operator is to first calculate them in the space fixed reference frame and then to project them onto the molecule fixed axes using the direction cosine matrix elements [see Eq. (10-5)]. For example,

$$\hat{J}_x = \lambda_{x\xi}\hat{J}_\xi + \lambda_{x\eta}\hat{J}_\eta + \lambda_{x\zeta}\hat{J}_\zeta. \tag{10-83}$$

Using this equation and the similar ones for the $\hat{J}_y$ and $\hat{J}_z$ components we obtain the required relations as follows:

$$\hat{J}_x = \sin\chi\hat{P}_\theta - \csc\theta\cos\chi\hat{P}_\phi + \cot\theta\cos\chi\hat{P}_\chi, \tag{10-84}$$

$$\hat{J}_y = \cos\chi\hat{P}_\theta + \csc\theta\sin\chi\hat{P}_\phi - \cot\theta\sin\chi\hat{P}_\chi, \tag{10-85}$$

and

$$\hat{J}_z = \hat{P}_\chi. \tag{10-86}$$

The square of the rovibronic angular momentum is given by

$$\begin{aligned}\hat{\boldsymbol{J}}^2 &= \hat{J}_x{}^2 + \hat{J}_y{}^2 + \hat{J}_z{}^2\\ &= \hat{J}_\xi{}^2 + \hat{J}_\eta{}^2 + \hat{J}_\zeta{}^2.\end{aligned} \tag{10-87}$$

The operator representing the square of the rovibronic angular momentum $\hat{\boldsymbol{J}}^2$ commutes with each of the components of $\hat{\boldsymbol{J}}$ about the (ξ, η, ζ) axes. Thus we can have eigenfunctions that are simultaneously eigenfunctions of $\hat{\boldsymbol{J}}^2$ and any one component; we choose $\hat{J}_\zeta$. Further, the rovibronic Hamiltonian $\hat{H}_{\rm rve}$ commutes with these operators, and thus the rovibronic wavefunctions $\Phi_{\rm rve}$ can be set up as simultaneous eigenfunctions of $\hat{H}_{\rm rve}$, $\hat{\boldsymbol{J}}^2$ and $\hat{J}_\zeta$. From the commutation relations of the space fixed components of the angular momentum operator it is possible to show that

$$\hat{\boldsymbol{J}}^2\Phi_{\rm rve} = J(J+1)\hbar^2\Phi_{\rm rve}, \tag{10-88}$$

and

$$\hat{J}_\zeta\Phi_{\rm rve} = m_J\hbar\Phi_{\rm rve}. \tag{10-89}$$

The rovibronic angular momentum quantum number J can have any positive integer value.[3] For a given value of J, the projection quantum number m_J can have any of the $(2J+1)$ values $-J, -J+1, \ldots, +J$. Each eigenstate $\Phi_{\rm rve}$ can be labeled by the rovibronic angular momentum quantum numbers J and m_J.

The rovibronic Hamiltonian commutes with the operations of $\boldsymbol{K}$(spatial), as discussed in Chapter 7, and the eigenfunction $\Phi_{\rm rve}(J, m_J)$ transforms according to the row labeled m_J in the irreducible representation $D^{(J)}$ of $\boldsymbol{K}$(spatial). Thus these eigenfunctions $\Phi_{\rm rve}$ transform *irreducibly* in $\boldsymbol{K}$(spatial).

Operators can also be set up to transform irreducibly in $\boldsymbol{K}$(spatial) [or in $\boldsymbol{K}$(mol); see Section 13.2.3] and when this is done they are called *irreducible spherical tensor operators.* By setting up operators in this way it becomes easy to evaluate their matrix elements in angular momentum eigenfunctions using the *Wigner-Eckart theorem* [see Eq. (14-24)]. This is made use of in Section 13.2.3 when we set up the rotation-vibration Hamiltonian of a spherical top molecule, in Chapter 14 when we determine the line strength of a transition, and many times in Chapter 16 [see also Chapter 5 of Zare (1988)]. The Hamiltonian operator transforms as the irreducible representation $D^{(0)}$ of $\boldsymbol{K}$(spatial) since it is invariant to any rotation operation of $\boldsymbol{K}$(spatial); it is a scalar with *rank* zero. An irreducible spherical tensor operator of rank k transforms according to $D^{(k)}$ and has $2k+1$ components; the dipole moment operator has rank 1, the quadrupole moment has rank 2, the octupole moment has rank 3, and so on. Since the Hamiltonian is a scalar it is expressible as the sum of scalars. Some of these scalar terms are built up by contracting two tensor operators of the same rank. An example is the term in the nuclear hyperfine Hamiltonian involving the contraction of the nuclear electric quadrupole moment operator and the operator giving the electric field gradient at that nucleus.

10.3.2 Angular momentum commutation properties

Once we have obtained the Hamiltonian as a function of the (x, y, z) components of $\boldsymbol{\hat{J}}$ it turns out to be very important in diagonalizing this Hamiltonian to know their commutation properties. The components of the rovibronic angular momentum about the (x, y, z) axes have different commutation properties from those of the components about the $\xi\eta\zeta$ axes. The components about the space fixed $\xi\eta\zeta$ axes obey the commutation relations

$$[\hat{J}_\sigma, \hat{J}_\tau] = +i\hbar \sum_\nu \varepsilon_{\sigma\tau\nu} \hat{J}_\nu, \qquad (10\text{-}90)$$

---

[3] **Angular momentum quantum numbers can also be half-integral. However, the rovibronic angular momentum quantum number (J for singlet states, but generally called N) is always integral.**

where $\sigma, \tau, \nu = \xi, \eta$, or ζ, and

$$\begin{aligned} \varepsilon_{\sigma\tau\nu} &= +1 \quad \text{if } \sigma\tau\nu \text{ are cyclic (i.e., } \xi\eta\zeta, \eta\zeta\xi, \text{ or } \zeta\xi\eta), \\ &= -1 \quad \text{if } \sigma\tau\nu \text{ are anticyclic (i.e., } \zeta\eta\xi, \eta\xi\zeta, \text{ or } \xi\zeta\eta), \\ &= \ \ 0 \quad \text{otherwise.} \end{aligned} \tag{10-91}$$

In contrast, the commutation relations of the components about the x, y and z axes are given by

$$[\hat{J}_\alpha, \hat{J}_\beta] = -i\hbar \sum_\gamma \varepsilon_{\alpha\beta\gamma} \hat{J}_\gamma, \tag{10-92}$$

where $\alpha, \beta, \gamma = x, y$, or z. The components of the rovibronic angular momentum about axes attached to the molecule (and which rotate as the molecule rotates) have commutation relations involving the opposite sign from that in the commutation relations of the components of the rovibronic angular momentum about axes with orientation fixed in space. It is said that the commutation relations of the molecule fixed components of the rovibronic angular momentum are 'anomalous.' It would be better to say simply that they are 'different.'

This difference in the commutation relations for the components of $\boldsymbol{J}$ about axes whose orientation remains fixed in space [the (ξ, η, ζ) axes], when compared to those about axes which rotate when the molecule rotates [the (x, y, z) axes], is not difficult to understand. It is straightforward algebra, and the reader can easily prove it using the expressions given in Eqs. (10-84)-(10-82). A simple geometrical analogy can be made by comparing the effect of successive rotations of a rigid body either about axes having orientation fixed in space, or about axes fixed to the body. In Fig. 4-3 we show that if we rotate a triangular prism about body fixed *abcd* axes we have the result

$$C_{3d}^2 C_{2a} = C_{2b}. \tag{10-93}$$

If the same starting orientation as used in Fig. 4-3 is used, but the orientation of the *abcd* axes are kept fixed in space, then we get the different result that

$$C_{3d}^2 C_{2a} = C_{2c}. \tag{10-94}$$

Using *abcd* axes with a fixed orientation in space gives a different multiplication table for the elements of the rotation group $\boldsymbol{D}_3$ from that obtained using molecule fixed axes (and given in Table 4-1). We could say that one of the multiplication tables is anomalous, but we do not.[4]

This is as much as we are going to say in this chapter about the (x, y, z) components of the rovibronic angular momentum. In the next chapter we will show how their commutation relations are used to determine rotational wavefunctions and important angular momentum matrix elements.

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[4] The change in the multiplication table has important implications for the way representations of the group are set up. See Bunker and Howard (1983), and the summary given in the Bibliographical Notes to Chapters 1 and 6.

10.3.3 Combining angular momentum operators

The nuclei and electrons in a molecule have spin angular momentum, and the way we combine (or add) these angular momentum operators to the rovibronic angular momentum operator is important. It is convenient to discuss this matter here even though this chapter is not supposed to be about spin. We have already mentioned spin in the discussion of the general Hamiltonian (Chapter 7), in the discussion of nuclear spin statistical weights (Chapter 8), and in the discussion of the Slater determinant used for the electronic basis wavefunctions (Chapter 9). We cannot write an equation like Eq. (10-79) for a spin angular momentum operator, but we can introduce equations like Eq. (10-87) for the square of a spin angular momentum operator. The spin angular momentum operators, like the rovibronic angular momentum operator, are all *vector* operators having components. The notation used for the various angular momentum operators is as follows:

$\hat{\boldsymbol{I}}_\alpha$	the spin angular momentum of nucleus α,
$\hat{\boldsymbol{s}}_i$	the spin angular momentum of electron i,
$\hat{\boldsymbol{I}}$	the total nuclear spin angular momentum in the molecule,
$\hat{\boldsymbol{S}}$	the total electron spin angular momentum in the molecule,
$\hat{\boldsymbol{T}}$	the total spin angular momentum in the molecule,
$\hat{\boldsymbol{L}}$	the total electronic orbital angular momentum in the molecule,
$\hat{\boldsymbol{N}}$	the rovibronic angular momentum in the molecule,
$\hat{\boldsymbol{J}}$	the sum of rovibronic and electron spin angular momenta, and
$\hat{\boldsymbol{F}}$	the total angular momentum.

As noted in Chapter 7 it is the accepted convention for electronic singlet states (when $\hat{\boldsymbol{J}} = \hat{\boldsymbol{N}}$) to use $\hat{\boldsymbol{J}}$ for the rovibronic angular momentum, and so we have used $\hat{\boldsymbol{J}}$ for the rovibronic angular momentum operator in the above subsections; in this subsection we use $\hat{\boldsymbol{N}}$. Having defined all these various angular momentum operators we now state some results concerning their eigenvalues and eigenfunctions, and the way we combine (or add) them.

Equations like Eq. (10-88) and (10-89) apply to all of these angular momentum operators, and we can write the general equations:

$$\hat{\boldsymbol{A}}^2|A,m_A\rangle = A(A+1)\hbar^2|A,m_A\rangle, \tag{10-95}$$

and

$$\hat{A}_\zeta|A,m_A\rangle = m_A\hbar|A,m_A\rangle, \tag{10-96}$$

where we use the ket notation $|A,m_A\rangle$ to symbolize the simultaneous eigenfunction of the square $\hat{\boldsymbol{A}}^2$ and ζ component $\hat{A}_\zeta$ of the angular momentum operator $\hat{\boldsymbol{A}}$. For spins the quantum number A can be integral or half integral, and so the quantum numbers I, S, T, J and F can be integral or half integral (N is always integral). The projection quantum number m_A runs over the $2A+1$ values $-A$, $-A+1$, $-A+2$, $\ldots$, $+A$.

Adding (or coupling) vector operators, and constructing linear combinations of product eigenfunctions, is an important area of angular momentum theory. By definition

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{S}} + \hat{\boldsymbol{N}}, \tag{10-97}$$

and as a result each eigenstate $|J, m_J\rangle$ describes a compound system that involves both rovibronic and electron spin angular momenta. Such a compound state can be described by simple (uncoupled) product functions $|N, m_N\rangle|S, m_S\rangle$ that are simultaneous eigenfunctions of the four commuting operators $\hat{\boldsymbol{N}}^2$, $\hat{N}_\zeta$, $\hat{\boldsymbol{S}}^2$, and $\hat{S}_\zeta$. Or we can form the (coupled) functions $|J, m_J\rangle$ that are simultaneous eigenfunctions of $\hat{\boldsymbol{J}}^2$ $[= (\hat{\boldsymbol{N}} + \hat{\boldsymbol{S}})^2]$, $\hat{J}_\zeta$ $(= \hat{N}_\zeta + \hat{S}_\zeta)$, $\hat{\boldsymbol{N}}^2$, and $\hat{\boldsymbol{S}}^2$. The coupled functions can be written as linear combinations of the uncoupled functions:

$$\begin{aligned} |J, m_J\rangle &= \sum_{m_N, m_S} C(NSJ; m_N m_S m_J)|N, m_N\rangle|S, m_S\rangle \\ &= \sum_{m_N, m_J} (-1)^{N-S+m_J}\sqrt{2J+1}\begin{pmatrix} N & S & J \\ m_N & m_S & -m_J \end{pmatrix}|N, m_N\rangle|S, m_S\rangle, \end{aligned} \tag{10-98}$$

where

$$\begin{pmatrix} N & S & J \\ m_N & m_S & -m_J \end{pmatrix}$$

is a $3j$-symbol, and $C(NSJ; m_N m_s m_J)$ is called a Clebsch-Gordan coefficient. These factors are chosen to be real, and the expressions for them are well known; in any application they would normally be calculated numerically [see, for example, the Appendix of Zare (1988)]. For the coupled functions the quantum number J is restricted to the values from $|N-S|$ to $N+S$, and for each J there are the $(2J+1)$ values for the projection quantum number m_J. This result is an expression of Eq. (7-44): the $(2N+1)$ functions $|N, m_N\rangle$ transform as the representation $D^{(N)}$ of the group $\boldsymbol{K}$(spatial), the $(2S+1)$ functions $|S, m_S\rangle$ transform as the representation $D^{(S)}$ of the group $\boldsymbol{K}$(spatial), and the resultant functions $|J, m_J\rangle$ transform as the representation $D^{(N)} \otimes D^{(S)}$ of the group $\boldsymbol{K}$(spatial). The Clebsch-Gordan coefficients form appropriate sums of the uncoupled functions so that the coupled functions transform irreducibly, and they can be used to determine the coefficients of the irreducible representations in the product representation. Any two angular momentum operators generate coupled or uncoupled eigenfunctions that are related by Eq. (10-98).

The total angular momentum operator $\hat{\boldsymbol{F}}$ is given by

$$\hat{\boldsymbol{F}} = \hat{\boldsymbol{I}} + \hat{\boldsymbol{S}} + \hat{\boldsymbol{N}}. \tag{10-99}$$

and this involves the coupling of three angular momentum operators. However, now there is more than one way to do the coupling. We could first couple $\hat{\boldsymbol{S}}$ and $\hat{\boldsymbol{N}}$ to form $\hat{\boldsymbol{J}}$, and then couple $\hat{\boldsymbol{J}}$ and $\hat{\boldsymbol{I}}$ to form $\hat{\boldsymbol{F}}$ (the eigenfunctions would be labeled $|I, J, F, m_F\rangle$), or we could first couple $\hat{\boldsymbol{I}}$ and $\hat{\boldsymbol{S}}$ to form $\hat{\boldsymbol{T}}$, and then couple $\hat{\boldsymbol{T}}$ and $\hat{\boldsymbol{N}}$ to form $\hat{\boldsymbol{F}}$ (the eigenfunctions would be labeled $|T, N, F, m_F\rangle$). The two different sets of coupled eigenfunctions are related by

$$\begin{aligned}|I, J, F, m_F\rangle &= \sum_T \sqrt{(2T+1)(2J+1)}W(ISFN;TJ)|T, N, F, m_F\rangle \\ &= \sum_T (-1)^{I+S+N+F}\sqrt{(2T+1)(2J+1)} \\ &\times \left\{ \begin{matrix} I & S & T \\ N & F & J \end{matrix} \right\} |T, N, F, m_F\rangle, \qquad (10\text{-}100)\end{aligned}$$

where

$$\left\{ \begin{matrix} I & S & T \\ N & F & J \end{matrix} \right\}$$

is a $6j$-symbol, and $W(ISFN;TJ)$ is a Racah coefficient (these are sometimes called recoupling coefficients). These coefficients are discussed further in Zare (1988), for example. Higher nj-symbols can be defined by considering the recoupling of more angular momenta.

10.4 THE NORMAL COORDINATES

The classical vibrational kinetic energy expression involves the velocities of the Cartesian displacement coordinates, and the potential energy depends on bond length and bond angle displacements from equilibrium. Clearly we have to find one set of coordinates for both. The most commonly chosen vibrational coordinates are the normal coordinates which are linear functions of the Cartesian displacement coordinates that approximate bond length and bond angle displacements in the limit of infinitesimal amplitudes. In this section we explain how the normal coordinates are defined. Whereas the Eckart equations are used to define the (x, y, z) axes with the aim of minimizing rotation-vibration coupling in the rotation-vibration Hamiltonian, the normal coordinates are introduced with the aim of minimizing inter-mode coupling in the vibrational Hamiltonian.

10.4.1 The classical vibrational energy

The derivation of the vibrational Hamiltonian begins with the classical vibrational energy, and we have to discuss the kinetic and potential energy expressions separately. From the seventh term in Eq. (8) in Section 11-1 of the book by Wilson, Decius and Cross (1955), the classical expression for the vibrational kinetic energy in the molecule fixed (x, y, z) axis system is given in terms of the Cartesian displacement coordinate velocities as

$$T_{\text{vib}} = \frac{1}{2}\sum_{i=1}^{N} m_i \left[\left(\frac{d\Delta x_i}{dt}\right)^2 + \left(\frac{d\Delta y_i}{dt}\right)^2 + \left(\frac{d\Delta z_i}{dt}\right)^2\right], \tag{10-101}$$

where m_i is the mass of nucleus i. There are six constraints on the $\Delta\alpha_i$ given by Eqs. (10-70)-(10-73).

The potential energy function V_{N} [see Eqs. (9-55) and (9-61)] is expressed as a function of the displacements from equilibrium of the internal coordinates of the molecule (bond lengths and bond angles). It has the value zero if the nuclei are in their equilibrium configuration when these displacement coordinates are zero, and we choose to expand V_{N} as a Taylor series in the displacements of these internal coordinates from their equilibrium values. We use the symbol $\mathcal{R}_i$ for the $(3N-6)$ independent internal displacement coordinates and write [see Hoy, Mills and Strey (1972)]

$$V_{\text{N}} = \frac{1}{2}\sum_{ij} f_{ij}\mathcal{R}_i\mathcal{R}_j + \frac{1}{6}\sum_{ijk} f_{ijk}\mathcal{R}_i\mathcal{R}_j\mathcal{R}_k + \frac{1}{24}\sum_{ijkl} f_{ijkl}\mathcal{R}_i\mathcal{R}_j\mathcal{R}_k\mathcal{R}_l + \cdots . \tag{10-102}$$

The *force constants* f_{ij}, f_{ijk}, and f_{ijkl} are second, third, and fourth derivatives (at equilibrium) of V_{N} with respect to the coordinates $\mathcal{R}_i$. Generally Eq. (10-102) is not taken beyond quartic terms.

As an example, for a water molecule, there are three internal coordinates $\mathcal{R}_1$, $\mathcal{R}_2$, and $\mathcal{R}_3$, and we normally choose them as

$$\begin{bmatrix} \mathcal{R}_1 \\ \mathcal{R}_2 \\ \mathcal{R}_3 \end{bmatrix} = \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta\theta \end{bmatrix} = \begin{bmatrix} r_1 - r_e \\ r_2 - r_e \\ \theta - \theta_e \end{bmatrix}, \tag{10-103}$$

where r_1 and r_2 are the two OH bond lengths (and r_e is their common equilibrium value), and $\theta = \angle\,(\text{HOH})$ is the bond angle with equilibrium value θ_e. That is, for a water molecule, Eq. (10-102) (truncated after the third order terms) becomes

$$\begin{aligned} V_{\text{N}}(\Delta r_1, \Delta r_2, \Delta\theta) = {} & \frac{1}{2}f_{rr}\left(\Delta r_1^2 + \Delta r_2^2\right) + \frac{1}{2}f_{\theta\theta}\Delta\theta^2 + f_{rr'}\Delta r_1\Delta r_2 \\ & + f_{r\theta}\left(\Delta r_1 + \Delta r_2\right)\Delta\theta + \frac{1}{6}f_{rrr}\left(\Delta r_1^3 + \Delta r_2^3\right) \\ & + \frac{1}{6}f_{\theta\theta\theta}\Delta\theta^3 + \frac{1}{2}f_{rr\theta}\left(\Delta r_1^2 + \Delta r_2^2\right)\Delta\theta \\ & + \frac{1}{2}f_{r\theta\theta}\left(\Delta r_1 + \Delta r_2\right)\Delta\theta^2 + \frac{1}{2}f_{rrr'}\left(\Delta r_1^2\Delta r_2 + \Delta r_1\Delta r_2^2\right) \\ & + f_{rr'\theta}\Delta r_1\Delta r_2\Delta\theta + \ldots , \end{aligned} \tag{10-104}$$

where we have taken into account that the two OH bond lengths are equivalent so that for water, V_{N} is unchanged by the interchange of Δr_1 and Δr_2.

When we express V_N in terms of the internal $\mathcal{R}_i$ coordinates, the parameters of Eq. (10-102) [i.e., the force constants f_{ij}, f_{ijk}, and f_{ijkl}] are *isotope independent* in that they are the same for all isotopomers of a given molecule. The reason is that V_N is obtained by diagonalizing the electronic Hamiltonian [Eq. (9-63)] which does not contain the masses of the nuclei.

The addition of V_N from Eq. (10-102) to $T_{\rm vib}$ from Eq. (10-101) gives the classical vibrational energy $E_{\rm vib}$.

10.4.2 The linearized internal coordinates S_i

The expressions for V_N and $T_{\rm vib}$ given above depend on different coordinates, so in order that we can use $E_{\rm vib}$ to generate a quantum mechanical Hamiltonian for vibration, we must transform to a common set of coordinates. We first note that in general, the $\mathcal{R}_i$ are nonlinear functions of the Cartesian displacement coordinates $\Delta\alpha_k, \Delta\beta_k$, etc., and they are written as

$$\begin{aligned}\mathcal{R}_i &= \sum_\alpha \sum_k B_i^{\alpha k}\Delta\alpha_k + \frac{1}{2}\sum_{\alpha,\beta}\sum_{k,n} B_i^{\alpha k,\beta n}\Delta\alpha_k\Delta\beta_n \\ &\quad + \frac{1}{6}\sum_{\alpha,\beta,\gamma}\sum_{k,n,p} B_i^{\alpha k,\beta n,\gamma p}\Delta\alpha_k\Delta\beta_n\Delta\gamma_p + \cdots, \qquad (10\text{-}105)\end{aligned}$$

where α, β and γ run over x, y and z, and k, n and p run from 1 to N. The coefficients $B_i^{\alpha k}, B_i^{\alpha k,\beta n}$, and $B_i^{\alpha k,\beta n,\gamma p}$ are elements of the so-called $\boldsymbol{B}$ tensor and they are given by the first, second, and third derivatives (at equilibrium) of $\mathcal{R}_i$ with respect to the Cartesian displacement coordinates. These elements only depend on the equilibrium molecular geometry; the first derivatives $B_i^{\alpha k}$ are the elements of the so-called B matrix [it is a $(3N-6)\times 3N$-dimensional matrix].

We now define a set of $3N-6$ *linearized internal coordinates* S_i as

$$S_i = \sum_\alpha\sum_k B_i^{\alpha k}\Delta\alpha_k = \sum_\alpha\sum_k\left(\frac{\partial\mathcal{R}_i}{\partial\Delta\alpha_k}\right)_{\rm eq}\Delta\alpha_k, \qquad (10\text{-}106)$$

where we have indicated that the B matrix elements are the derivatives of the $\mathcal{R}_i$ coordinates with respect to the $\Delta\alpha_k$ displacements, taken at the equilibrium configuration. The coordinate S_i is, by definition, given as the first-order Taylor expansion of $\mathcal{R}_i$ in terms of the $\Delta\alpha_k$, and so for small $\Delta\alpha_k$ values

$$S_i \approx \mathcal{R}_i. \qquad (10\text{-}107)$$

The B-matrix elements $B_i^{\alpha k} = (\partial\mathcal{R}_i/\partial\Delta\alpha_k)_{\rm eq}$ can be obtained from purely geometrical considerations. We consider as an example the water molecule drawn in Fig. 10-2. For the internal coordinate $\mathcal{R}_1 = \Delta r_1 = r_1 - r_e$, where r_1 is the distance from the hydrogen nucleus labeled 1 to the oxygen nucleus (labeled 3), we have

$$\Delta r_1 = \sqrt{\sum_{\alpha=x,y,z} (\alpha_1{}^e + \Delta\alpha_1 - \alpha_3{}^e - \Delta\alpha_3)^2} - r_e, \tag{10-108}$$

so that for example

$$B_1^{x\,1} = \left(\frac{\partial \mathcal{R}_1}{\partial \Delta x_1}\right)_{\text{eq}} = \frac{x_1{}^e - x_3{}^e}{\sqrt{\sum_{\alpha=x,y,z} (\alpha_1{}^e - \alpha_3{}^e)^2}} = \frac{x_1{}^e - x_3{}^e}{r_e}. \tag{10-109}$$

Inspection of Fig. 10-2 shows that

$$B_1^{x\,1} = -\cos\left(\frac{\theta_e}{2}\right). \tag{10-110}$$

In general, B-matrix elements can be derived from geometrical arguments of the type employed here [see Hoy, Mills, and Strey (1972)].

The linearized internal coordinates S_i are related to the displacement coordinates $\Delta\alpha_k$ through the linear equations (10-106), and we aim at using these relations to transform the kinetic energy in Eq. (10-101) to a form that depends on the S_i coordinates. We must obtain the $\Delta\alpha_k$ coordinates in terms of the S_i. This cannot be done by inverting Eq. (10-106) in a straightforward manner, because the $3N$ displacements $\Delta\alpha_k$ are not all independent. They fulfill the center of mass equations (10-73) and the Eckart equations (10-70)-(10-72). We define three *translational coordinates*

$$T_\alpha = M_{\text{N}}^{-1/2} \sum_{i=1}^{N} m_i^{1/2}(m_i^{1/2}\Delta\alpha_i), \tag{10-111}$$

where M_{N} is the total mass of all the nuclei in the molecule, and three *rotational coordinates* R_x, R_y, and R_z, where

$$R_x = (\mu_{xx}^e)^{1/2} \sum_{i=1}^{N} m_i^{1/2}[y_i{}^e(m_i^{1/2}\Delta z_i) - z_i{}^e(m_i^{1/2}\Delta y_i)], \tag{10-112}$$

with $\mu_{xx}^e = \{\sum_i m_i[(y_i{}^e)^2 + (z_i{}^e)^2]\}^{-1}$ [see below]. The expressions for R_y and R_z are obtained by cyclically permuting xyz in Eq. (10-112). The numerical factors in Eqs. (10-111) and (10-112) are convenient for reasons to be discussed below. The coordinates S_i [$i = 1, 2, 3, \ldots, 3N-6$], T_α, and R_α [$\alpha = x, y, z$], are related to the displacements $\Delta\alpha_k$ by the matrix equation

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ \vdots \\ S_{3N-6} \\ T_x \\ T_y \\ T_z \\ R_x \\ R_y \\ R_z \end{bmatrix} = \begin{bmatrix} \\ \\ B \\ \\ \\ \cdots\cdots\cdots\cdots \\ \\ \\ B_{\text{cond}} \\ \\ \\ \\ \end{bmatrix} \begin{bmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \Delta x_2 \\ \Delta y_2 \\ \vdots \\ \Delta x_{N-1} \\ \Delta y_{N-1} \\ \Delta z_{N-1} \\ \Delta x_N \\ \Delta y_N \\ \Delta z_N \end{bmatrix}. \tag{10-113}$$

In Eq. (10-113), B is the $(3N-6) \times 3N$-dimensional matrix with elements $B_i^{\alpha k} = (\partial\mathfrak{R}_i/\partial\Delta\alpha_k)_{\text{eq}}$, and B_{cond} is a $6 \times 3N$-dimensional matrix whose elements can be identified from Eqs. (10-111) and (10-112).

We have defined the translational coordinates T_x, T_y, and T_z to be proportional to those three combinations of Cartesian displacement coordinates $\Delta\alpha_i$ that vanish as a result of the center of mass condition [Eq. (10-73)], and the rotational coordinates R_x, R_y, and R_z to be proportional to to those combinations of $\Delta\alpha_i$ that vanish using Eckart conditions [Eq. (10-70)-(10-72)]. That is, we can set

$$T_x = T_y = T_z = R_x = R_y = R_z = 0. \tag{10-114}$$

The total coefficient matrix of Eq. (10-113), obtained by combining the matrices B and B_{cond} as indicated in the equation, is $3N \times 3N$-dimensional [i.e., square] and can be inverted. Thus, having inserted Eq. (10-114) in Eq. (10-113), we can invert this equation to obtain the $\Delta\alpha_k$ in terms of the S_i. With the resulting relations we can transform the kinetic energy of Eq. (10-101) to make it depend on the S_i coordinates. The result is

$$T_{\text{vib}} = \frac{1}{2}\frac{\widetilde{d\boldsymbol{S}}}{dt}\boldsymbol{G}^{-1}\frac{d\boldsymbol{S}}{dt}, \tag{10-115}$$

where $\boldsymbol{S}$ is a $(3N-6)$-component column vector containing the coordinates S_1, S_2, S_3, $\ldots$, S_{3N-6}, and $\widetilde{d\boldsymbol{S}/dt}$ denotes the transpose of $d\boldsymbol{S}/dt$ [see Table 5-1]. In Eq. (10-115), the $(3N-6) \times (3N-6)$-dimensional matrix $\boldsymbol{G}^{-1}$ is the inverse of

$$\boldsymbol{G} = BM^{-1}\tilde{B}, \tag{10-116}$$

where M is a $3N \times 3N$-dimensional diagonal matrix of the nuclear masses[5] with $M_{11} = M_{22} = M_{33} = m_1$, $M_{44} = M_{55} = M_{66} = m_2$, $M_{77} = M_{88} = M_{99} = m_4$, and so on.

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[5] But see the last paragraph in this chapter for the justification of always using atomic masses here

From Eqs. (10-102), (10-105) and (10-106) the ***harmonic potential function*** V_{harm} is given by

$$V_{\mathrm{harm}} = \frac{1}{2}\sum_{ij} f_{ij} S_i S_j = \frac{1}{2}\tilde{\boldsymbol{S}}\boldsymbol{F}\boldsymbol{S}, \tag{10-117}$$

where the $(3N-6) \times (3N-6)$-dimensional matrix $\boldsymbol{F}$ contains the quadratic force constants f_{ij}. For a water molecule, this matrix is given by

$$\boldsymbol{F} = \begin{bmatrix} f_{rr} & f_{rr'} & f_{r\theta} \\ f_{rr'} & f_{rr} & f_{r\theta} \\ f_{r\theta} & f_{r\theta} & f_{\theta\theta} \end{bmatrix}. \tag{10-118}$$

We now have the expression for the total classical vibrational energy (in the harmonic approximation) as

$$E^0_{\mathrm{vib}} = T_{\mathrm{vib}} + V_{\mathrm{harm}} = \frac{1}{2}\widetilde{\frac{d\boldsymbol{S}}{dt}}\boldsymbol{G}^{-1}\frac{d\boldsymbol{S}}{dt} + \frac{1}{2}\tilde{\boldsymbol{S}}\boldsymbol{F}\boldsymbol{S}, \tag{10-119}$$

in which the kinetic and potential energies are both expressed in terms of the S_i coordinates. This expression is approximate since we have truncated the expression for the potential energy after the second-order terms. The elements of the $\boldsymbol{F}$ matrix are the harmonic force constants, and the elements of the $\boldsymbol{G}$ matrix depend on the atomic masses and the equilibrium bond lengths and angles. Formulas for $\boldsymbol{G}$ matrix elements are tabulated in Appendix VI of Wilson, Decius and Cross (1955).

10.4.3 The introduction of the normal coordinates

We now use a standard method from classical mechanics, the *GF calculation*, to express E^0_{vib} as the sum of $3N-6$ independent terms, each term depending on one so-called ***normal coordinate*** Q_r only. In this way, we can eventually separate the Schrödinger equation in the harmonic approximation for the vibration of the molecule into $3N-6$ independent, one-dimensional Schrödinger equations. The idea is to make a further coordinate transformation defined by

$$\boldsymbol{S} = \boldsymbol{L}\boldsymbol{Q} \tag{10-120}$$

where $\boldsymbol{L}$ is a $(3N-6) \times (3N-6)$-dimensional coefficient matrix with constant matrix elements [i.e., the $\boldsymbol{L}$ matrix elements are time-independent], and $\boldsymbol{Q}$ is a $(3N-6)$-component column vector containing the normal coordinates Q_1, Q_2, Q_3, ..., Q_{3N-6}. The $\boldsymbol{L}$ matrix is defined so that we can write the kinetic energy as

$$T_{\mathrm{vib}} = \frac{1}{2}\sum_{r=1}^{3N-6}\left(\frac{dQ_r}{dt}\right)^2 = \frac{1}{2}\widetilde{\frac{d\boldsymbol{Q}}{dt}}\frac{d\boldsymbol{Q}}{dt} \tag{10-121}$$

and the harmonic potential energy as

$$V_{\text{harm}} = \frac{1}{2}\sum_{r=1}^{3N-6} \lambda_r Q_r^2 = \frac{1}{2}\tilde{\boldsymbol{Q}}\Lambda\boldsymbol{Q}, \tag{10-122}$$

where the λ_r are constants and Λ is a $(3N-6)\times(3N-6)$-dimensional diagonal matrix with $\Lambda_{rr} = \lambda_r$, $r = 1, 2, 3, \ldots, 3N-6$.

If we insert Eq. (10-120) in Eq. (10-115) we obtain

$$T_{\text{vib}} = \frac{1}{2}\widetilde{\left(L\frac{d\boldsymbol{Q}}{dt}\right)}\boldsymbol{G}^{-1}L\frac{d\boldsymbol{Q}}{dt}, = \frac{1}{2}\frac{d\widetilde{\boldsymbol{Q}}}{dt}\left(\tilde{L}\boldsymbol{G}^{-1}L\right)\frac{d\boldsymbol{Q}}{dt}, \tag{10-123}$$

and in order that Eq. (10-121) be fulfilled, we must have from Eq. (10-123)

$$\tilde{L}\boldsymbol{G}^{-1}L = \boldsymbol{E}, \tag{10-124}$$

where $\boldsymbol{E}$ is a $(3N-6)\times(3N-6)$-dimensional unit matrix. We can also insert Eq. (10-120) in Eq. (10-117) for V_{harm}, and thus for Eqs. (10-117) and (10-122) to be fulfilled simultaneously, we must have

$$\tilde{L}\boldsymbol{F}L = \Lambda. \tag{10-125}$$

From Eq. (10-124) we derive

$$\tilde{L} = L^{-1}\boldsymbol{G}, \tag{10-126}$$

which is inserted in Eq. (10-125) to yield

$$L^{-1}\boldsymbol{G}\boldsymbol{F}L = \Lambda. \tag{10-127}$$

This equation is analogous to the matrix eigenvalue equation Eq. (6-162). That is, λ_r is the r'th eigenvalue of the matrix $\boldsymbol{GF}$, and the r'th column of L is the associated eigenvector. Hence we can solve Eq. (10-127) for L and Λ by means of standard computational methods for matrix diagonalization. The columns of the calculated L matrix must be normalized so that [Eq. (10-126)]

$$L\tilde{L} = \boldsymbol{G}. \tag{10-128}$$

In terms of the normal coordinates Q_r, the classical harmonic vibrational energy is

$$E_{\text{vib}}^0 = \frac{1}{2}\sum_{r=1}^{3N-6}\left[\left(\frac{dQ_r}{dt}\right)^2 + \lambda_r Q_r^2\right]. \tag{10-129}$$

If the molecule were described by the laws of classical mechanics, it would be able to carry out a vibration where one normal coordinate Q_r varies periodically in time, while all the other coordinates Q_s, $s \neq r$, are fixed at zero. This motion is called a ***normal mode***. From Eq. (9-17) the classical momentum conjugate to Q_r is given by

$$P_r = \frac{\partial(T_{\text{vib}} - V_{\text{harm}})}{\partial\dot{Q}_r} = \dot{Q}_r, \tag{10-130}$$

where $\dot{Q}_r = dQ_r/dt$. Thus in terms of normal coordinates Q_r and their conjugate momenta P_r the classical harmonic vibrational energy is

$$E^0_{\text{vib}} = \frac{1}{2}\sum_{r=1}^{3N-6}\left[P_r^2 + \lambda_r Q_r^2\right], \tag{10-131}$$

and the quantum mechanical harmonic vibrational Hamiltonian is

$$\hat{H}^0_{\text{vib}} = \frac{1}{2}\sum_{r=1}^{3N-6}\left[\hat{P}_r^2 + \lambda_r Q_r^2\right]. \tag{10-132}$$

where $\hat{P}_r = -i\hbar\partial/\partial Q_r$. We will discuss the eigenvalues and eigenfunctions of this vibrational Hamiltonian in Chapter 11.

The harmonic vibrational Hamiltonian is of course approximate, and we want to express the complete rotation-vibration Hamiltonian

$$\hat{H}_{\text{rv}} = \hat{T}_{\text{N}} + \hat{V}_{\text{N}} \tag{10-133}$$

in Eq. (9-60) in terms of the Euler angles (actually the (x, y, z) components of the rovibronic angular momentum) and the normal coordinates. The relation between the Cartesian displacement coordinates and the normal coordinates is where the l matrix comes in. This relation is straightforward since we have already inverted Eq. (10-113) to express the $\Delta\alpha_k$ coordinates in terms of the linearized internal coordinates S_i, and these depend linearly on the Q_r as given by Eq. (10-120). The linear relationship between the $\Delta\alpha_k$ and the Q_r defines the l matrix according to

$$\begin{bmatrix} m_1^{1/2}\Delta x_1 \\ \\ \vdots \\ \\ m_N^{1/2}\Delta z_N \end{bmatrix} = \begin{bmatrix} \\ \\ l_{\alpha i,r} \\ \\ \\ \end{bmatrix} \begin{bmatrix} Q_1 \\ \vdots \\ Q_{3N-6} \\ T_x \\ \vdots \\ R_z \end{bmatrix}. \tag{10-134}$$

This equation relates the $3N$ mass-weighted displacement coordinates $m_k^{1/2}\Delta\alpha_k$ to a set of $3N$ coordinates comprising the $3N-6$ normal coordinates Q_r, the three translational coordinates T_x, T_y, and T_z defined by Eq. (10-111), and the three rotational coordinates R_x, R_y, and R_z defined by Eq. (10-112). It can be shown that by mass-weighting the displacement coordinates as indicated, and by letting the definitions of the translational and rotational coordinates contain the numerical factors given in Eqs. (10-111) and (10-112), respectively, we obtain a particularly simple form of the $3N \times 3N$-dimensional l matrix in that this matrix becomes orthogonal, satisfying

$$\sum_{\alpha} \sum_{i=1}^{N} l_{\alpha i,r} l_{\alpha i,s} = \delta_{rs}. \tag{10-135}$$

We call the six T_α and R_α *zero frequency normal coordinates* and write

$$[R_x, R_y, R_z, T_x, T_y, T_z] = [Q_{3N-5}, Q_{3N-4}, \ldots, Q_{3N}]. \tag{10-136}$$

In connection with Eq. (10-114), we have already argued that the center of mass condition [Eq. (10-73)] and the Eckart conditions [Eq. (10-70)-(10-72)]. demand that the zero frequency normal coordinates vanish. Hence, we can rewrite Eq. (10-134) as

$$\Delta\alpha_i = \sum_{r=1}^{3N-6} m_i^{-1/2} l_{\alpha i,r} Q_r. \tag{10-137}$$

The "left" $3N \times (3N-6)$-dimensional part of the l matrix [that is, the part needed in Eq. (10-137)], can be expressed in terms of the matrices encountered in the GF calculation [Crawford and Fletcher (1951)]. If we denote this $3N \times (3N-6)$-dimensional matrix block by l_Q, we have

$$l_Q = M^{-1/2} \tilde{B} \boldsymbol{G}^{-1} L. \tag{10-138}$$

With Eq. (10-137), we can transform the kinetic energy operator $\hat{T}_{\mathrm{N}}$ for the rotation and vibration to depend on the normal coordinates Q_r. We would like to transform the operator for the potential energy, V_{N}, in an analogous manner. However, V_{N} is expressed as a function of the internal coordinates $\mathfrak{R}_i$ [Eq. (10-102)], and we must express these in terms of the normal coordinates in order that we can carry out the desired transformation. This can be done by inserting Eq. (10-137) in Eq. (10-105). The result is

$$\mathfrak{R}_i = \sum_r L_{ir} Q_r + \frac{1}{2} \sum_{r,s} L_{irs} Q_r Q_s + \frac{1}{6} \sum_{r,s,t} L_{irst} Q_r Q_s Q_t + \cdots, \tag{10-139}$$

where the L_{ir} are the elements of the L matrix. All the expansion coefficients L_{ir}, L_{irs}, and L_{irst}, ... are said to be elements of the so-called $\boldsymbol{L}$ tensor. The higher $\boldsymbol{L}$ tensor elements L_{irs}, L_{irst}, ..., can all be expressed in terms of the L_{ir} [see the discussion above Eq. (20) in Hoy, Mills, and Strey (1972)]. Substituting Eq. (10-139) into Eq. (10-102) yields

$$V_{\mathrm{N}} = \frac{1}{2} \sum_{r,s} \Phi_{rs} Q_r Q_s + \frac{1}{6} \sum_{r,s,t} \Phi_{rst} Q_r Q_s Q_t + \frac{1}{24} \sum_{r,s,t,u} \Phi_{rstu} Q_r Q_s Q_t Q_u + \cdots, \tag{10-140}$$

where

$$\Phi_{rs} = \sum_{i,j} L_{ir} f_{ij} L_{js} \tag{10-141}$$

and Φ_{rst} and Φ_{rstu} are given by more complicated expressions involving the higher order force constants f_{ijk}, f_{ijkl}, . . . , and the elements of the $\boldsymbol{L}$ tensor. The quantity Φ_{rs} in Eq. (10-141) is an element of the matrix $\tilde{L}\boldsymbol{F}L$, and it follows from Eq. (10-125) that we have chosen the L matrix elements so that

$$\Phi_{rs} = \delta_{rs}\lambda_r, \tag{10-142}$$

i.e., so that Φ_{rs} is diagonal. This gives

$$V_{\mathrm{N}} = \frac{1}{2}\sum_r \lambda_r Q_r{}^2 + \frac{1}{6}\sum_{r,s,t} \Phi_{rst} Q_r Q_s Q_t + \frac{1}{24}\sum_{r,s,t,u} \Phi_{rstu} Q_r Q_s Q_t Q_u + \cdots. \tag{10-143}$$

The vibrational kinetic energy operator [see Eq. (10-132)] is given without approximation by

$$T_{\mathrm{vib}} = \frac{1}{2}\sum_r \hat{P}_r{}^2. \tag{10-144}$$

The simplicity of the kinetic energy operator is, of course, a direct result of the fact that the normal coordinates are simple linear functions of the Cartesian displacement coordinates.

10.4.4 A numerical example involving the normal coordinates

To determine the values of the normal coordinates from the Cartesian displacement coordinates given in Eq. (10-69) we use Eq. (10-137) and to do this we need the l_Q matrix from Eq. (10-138). We can obtain the l_Q matrix for the water molecule from the results in Hoy, Mills, and Strey (1972), and it is such that we can write Eq (10-137) for a deformed water molecule as

$$\begin{bmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \Delta x_2 \\ \Delta y_2 \\ \Delta z_2 \\ \Delta x_3 \\ \Delta y_3 \\ \Delta z_3 \end{bmatrix} = \begin{bmatrix} -0.3931 & 0.5414 & -0.4161 \\ 0 & 0 & 0 \\ -0.5742 & -0.4175 & -0.5423 \\ -0.3931 & 0.5414 & 0.4161 \\ 0 & 0 & 0 \\ 0.5742 & 0.4175 & -0.5423 \\ 0.0491 & -0.0677 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0.0678 \end{bmatrix} \begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \end{bmatrix} \tag{10-145}$$

where the $\Delta\alpha_i$ are in Å and the Q_r in $u^{1/2}$ Å. We can determine the values of the normal coordinates from this equation; for example, combining Eqs. (10-69) and (10-145) we have

$$\begin{aligned} \Delta x_1 &= -0.3931Q_1 \quad +0.5414Q_2 \quad -0.4161Q_3 &&= -0.8092, \\ \Delta x_3 &= 0.0491Q_1 \quad -0.0677Q_2 &&= +0.0491, \end{aligned}$$

and

$$\Delta z_3 = 0.0678Q_3 = +0.0678. \tag{10-146}$$

Inverting these three equations we determine that (in $u^{1/2}$ Å)

$$(Q_1, Q_2, Q_3) = (1, 0, 1). \tag{10-147}$$

Setting each $Q_i = 1\ u^{1/2}$ Å in turn in Eq. (10-145) the reader can determine the Cartesian displacement coordinates and picture the molecular deformation that each normal coordinate describes.

Thus for the deformed water molecule of Eq. (10-52) (see also Fig. 10-4) we have made the coordinate transformation from

$$(\xi_2, \eta_2, \zeta_2, \xi_3, \eta_3, \zeta_3) = (0.6760, 0.3138, 0.5614, -0.0930, 0.0360, 0.0872) \quad \text{in Å} \tag{10-148}$$

to

$$(\theta, \phi, \chi, Q_1, Q_2, Q_3) = (30°, 60°, 120°, 1u^{1/2}\text{Å}, 0, 1u^{1/2}\text{Å}) \tag{10-149}$$

by using the Eckart equations and the l matrix.

10.5 THE ROTATION-VIBRATION HAMILTONIAN

Using the Eckart equations and the l matrix in changing coordinates in the classical kinetic energy of Eq. (10-17), introducing the rovibronic angular momentum components, using the Podolsky trick to convert this to the quantum mechanical kinetic energy operator, and making Watson's simplification of this expression [Watson (1968)] the rotation-vibration kinetic energy operator expressed in terms of the $\hat{J}_\alpha$, $\hat{L}_\alpha$, Q_r and P_r is obtained as

$$\hat{T}_{\text{N}} = \frac{1}{2}\sum_{\alpha,\beta} \mu_{\alpha\beta}(\hat{J}_\alpha - \hat{p}_\alpha - \hat{L}_\alpha)(\hat{J}_\beta - \hat{p}_\beta - \hat{L}_\beta) + \frac{1}{2}\sum_{r} \hat{P}_r{}^2 + U, \tag{10-150}$$

where $\alpha = x$, y and z, $r = 1, 2, \ldots, (3N-6)$, the $\boldsymbol{\mu}$ matrix is the inverse of the $\boldsymbol{I}'$ matrix given in Eq. 10 on page 278 of Wilson, Decius, and Cross (1955) (the $\boldsymbol{I}'$ matrix is almost, but not quite, equal to the instantaneous inertia matrix $\boldsymbol{I}$ defined in Eqs. (10-31) and (10-32)), $\hat{J}_\alpha$ and $\hat{J}_\beta$ are components of the rovibronic angular momentum operator along the molecule fixed axes, and $\hat{p}_\alpha$ and $\hat{p}_\beta$ are referred to as components of the vibrational angular momentum operator [although they are not quite equal to the quantum mechanical counterparts of the components of J_{vib} given in Eq. (10-22)]. The $\hat{p}_\alpha$ are given by

$$\hat{p}_\alpha = \sum_{r,s} \zeta^\alpha_{r,s} Q_r \hat{P}_s, \tag{10-151}$$

where the $\zeta^\alpha_{r,s}$ (Coriolis coupling constants) depend on the l matrix according to

$$\zeta^x_{r,s} = -\zeta^x_{s,r} = \sum_{i=1}^{N} (l_{yi,r} l_{zi,s} - l_{zi,r} l_{yi,s}) \tag{10-152}$$

and cyclically for the y and z coefficients. The $\hat{L}_\alpha$ are the molecule fixed components of the electronic angular momentum. The term U is given by

$$U = -\frac{\hbar^2}{8} \sum_\alpha \mu_{\alpha\alpha}, \tag{10-153}$$

and it can be considered as a mass dependent contribution to the potential energy. The $\mu_{\alpha\beta}$ elements can be expressed as a Taylor series in the Q_r [Watson (1968)] as

$$\mu_{\alpha\beta} = \mu^e_{\alpha\beta} - \sum_r \mu^e_{\alpha\alpha} a_r^{\alpha\beta} \mu^e_{\beta\beta} Q_r + \frac{3}{4} \sum_{r,s,\gamma} \mu^e_{\alpha\alpha} a_r^{\alpha\gamma} \mu^e_{\gamma\gamma} a_s^{\gamma\beta} \mu^e_{\beta\beta} Q_r Q_s + \cdots, \tag{10-154}$$

where $\mu^e_{\alpha\beta} = \{[\mathbf{I}^e]^{-1}\}_{\alpha\beta}$ is an element of the inverse of the moment of inertia matrix for the molecule in its equilibrium configuration [from Eq. (10-33) only diagonal elements $\mu^e_{\alpha\alpha}$ are non-vanishing], and the coefficients $a_r^{\alpha\beta}$ depend on the equilibrium nuclear geometry, on the nuclear masses, and on the potential V_{N}. The expression for the potential energy V_{N} is given in Eq. (10-143).

In the *rigid rotor* approximation we retain only the first term in Eq. (10-154); for this to be an appropriate approximation the Q_r must be of small amplitude. As part of the Born-Oppenheimer separation of nuclear and electronic coordinates we neglect the electronic angular momenta in T_{N}. We neglect the vibrational angular momenta in T_{N}, which will be small as a result of having used the Eckart conditions. In the harmonic oscillator approximation we neglect all but the first term in the expression for V_{N} given in Eq. (10-143). Making all these approximations leads to the following rigid-rotor harmonic-oscillator Hamiltonian for the rotation-vibration motion

$$\hat{H}^0_{\text{rv}} = \frac{1}{2} \sum_\alpha \mu^e_{\alpha\alpha} \hat{J}_\alpha{}^2 + \frac{1}{2} \sum_r (\hat{P}_r{}^2 + \lambda_r Q_r{}^2). \tag{10-155}$$

This separates into a rigid-rotor Hamiltonian (the first term) and $(3N-6)$ separate harmonic oscillator Hamiltonians. The eigenfunctions of this separable Hamiltonian are used as basis functions for diagonalizing the complete rotation-vibration Hamiltonian.

As an afterthought it should be mentioned that although nuclear masses occur in the rotation-vibration Schrödinger equation [in the μ matrix elements and in the G matrix elements of Eq. (10-116)], it is better to use atomic masses in calculations in order to allow for the mass of the electrons; in fact, this partly allows for the breakdown of the Born-Oppenheimer approximation [see, for example, Eqs. (29)-(37) of Oka and Morino (1961)].

BIBLIOGRAPHICAL NOTES

The rotation-vibration Hamiltonian

Wilson and Howard (1936). The original derivation of the rotation-vibration Hamiltonian.

Darling and Dennison (1940). This paper gives a modification of the original derivation in order to ensure that the Hamiltonian is Hermitian.

Watson (1968). The rotation-vibration Hamiltonian is simplified for a nonlinear rigid polyatomic molecule.

Louck (1976). The rotation-vibration Hamiltonian of a polyatomic molecule is derived by Method I.

Papoušek and Aliev (1982). The rotation-vibration-electronic Hamiltonian of a polyatomic molecule is derived by Method II.

Angular momentum theory

Zare (1988). This is one of many books on angular momentum theory, and it refers to the others. It does discuss the application of angular momentum theory to molecules. The most difficult problems one faces in angular momentum algebra always involve ± signs. There are various places where a phase factor choice has to be made and different authors choose different ones; thus in making derivations one 'mixes' results from different authors at great peril. It is *extremely* important to know what phase conventions one is using and to use them consistently. We follow the phase conventions of Zare's book. Specifically a phase factor choice enters into the coupling equation Eq. (10-98), where the $3j$ symbols (and Clebsch-Gordan coefficients) are *real*, and in the definition of the rotational functions (see Eq. (11-13), noting the occurrence of complex conjugation, and Eq. (11-48)). Also the relative phases of the spin functions are chosen so that the matrix elements of the appropriate ladder operators are real and positive. Angular momentum theory is useful since one can calculate many complicated matrix elements by mindless manipulations involving relatively few basic equations. This is a result of the fact that we choose one set of $3j$ symbols (or Clebsch-Gordan coefficients) and couple all the angular momentum functions with them.

Kleiman, Gordon, Park, and Zare (1998). This book gives the solutions to all the problems in Zare (1988). It also lists errors in Zare (1988).

Brown and Howard (1976). This important paper discusses the application of spherical tensor methods to the calculation of matrix elements for molecules. However, be warned that the first ± sign on the lefthand side of Eq. (14) is a misprint; it should be a ∓ sign.

11

The Rotation and Vibration Wavefunctions

The rotation and vibration basis wavefunctions and energies for a rigid nonlinear molecule are obtained. The functions are rigid rotor rotational wavefunctions and harmonic oscillator vibrational wavefunctions; they are eigenfunctions of the rigid rotor and harmonic oscillator Hamiltonians. For the rigid rotor we discuss the spherical top, symmetric top and asymmetric top rotational wavefunctions and energies. For the harmonic oscillator we derive both the one-dimensional and two-dimensional (isotropic) harmonic oscillator vibrational wavefunctions and energies. Important matrix elements involving these basis functions are determined and tabulated. The commutators of the components of the rovibronic angular momentum, and of the vibrational normal coordinates and conjugate momenta, lead to the definition of 'ladder operators' for both the rotational and vibrational Hamiltonians. The use of these operators simplifies both the solution of the Schrödinger equations and the determination of the matrix elements. They also make it easy to determine the transformation properties of the wavefunctions under the effect of symmetry operations as we will see in Chapter 12.

11.1 INTRODUCTION

From Eqs. (10-143) and (10-150) the rotation-vibration Hamiltonian can be written [neglecting, as part of the Born-Oppenheimer approximation, the electronic angular momentum components $\hat{L}_\alpha$ and $\hat{L}_\beta$] as

$$\hat{H}_{\mathrm{rv}} = \frac{1}{2}\sum_\alpha \mu^{\mathrm{e}}_{\alpha\alpha}\hat{J}_\alpha{}^2 + \frac{1}{2}\sum_r(\hat{P}_r{}^2 + \lambda_r Q_r{}^2) \tag{11-1a}$$

$$+\frac{1}{2}\sum_{\alpha,\beta}(\mu_{\alpha\beta} - \mu^{\mathrm{e}}_{\alpha\beta})(\hat{J}_\alpha - \hat{p}_\alpha)(\hat{J}_\beta - \hat{p}_\beta) \tag{11-1b}$$

$$-\sum_\alpha \mu^{\mathrm{e}}_{\alpha\alpha}\hat{J}_\alpha\hat{p}_\alpha + \frac{1}{2}\sum_\alpha \mu^{\mathrm{e}}_{\alpha\alpha}\hat{p}_\alpha{}^2 \tag{11-1c}$$

$$+U + \frac{1}{6}\sum_{r,s,t}\Phi_{rst}Q_rQ_sQ_t + \frac{1}{24}\sum_{r,s,t,u}\Phi_{rstu}Q_rQ_sQ_tQ_u + \cdots . \tag{11-1d}$$

Equation (11-1a) is the sum of a rigid rotor Hamiltonian and of $(3N-6)$ harmonic oscillator Hamiltonians; the rest of the terms in Eq. (11-1) give rise to the effects of centrifugal distortion [Eq. (11-1b)], vibrational Coriolis coupling [Eq. (11-1c)], and anharmonicity [Eq. (11-1d)]. In this chapter we will determine the eigenfunctions of the separable Hamiltonian of Eq. (11-1a). These wavefunctions will be used to obtain the symmetry labels on the energy levels in the next chapter.

We write

$$\hat{H}^0_{\mathrm{rv}} = \frac{1}{2}\sum_{\alpha} \mu^{\mathrm{e}}_{\alpha\alpha} \hat{J}_{\alpha}{}^2 + \frac{1}{2}\sum_{r} (\hat{P}_r{}^2 + \lambda_r Q_r{}^2) \qquad (11\text{-}2)$$

and

$$\hat{H}^0_{\mathrm{rv}} \Phi^0_{\mathrm{rv}} = E^0_{\mathrm{rv}} \Phi^0_{\mathrm{rv}}. \qquad (11\text{-}3)$$

Because of the separation of the variables in $\hat{H}^0_{\mathrm{rv}}$, we have

$$\Phi^0_{\mathrm{rv}} = \Phi_{\mathrm{rot}}(\theta, \phi, \chi) \underbrace{\Phi_{v_1}(Q_1)\Phi_{v_2}(Q_2)\cdots}_{\Phi_{\mathrm{vib}}(Q_1, Q_2, \ldots)} \qquad (11\text{-}4)$$

and

$$E^0_{\mathrm{rv}} = E_{\mathrm{rot}} + \underbrace{E_{v_1} + E_{v_2} + \cdots}_{E_{\mathrm{vib}}}, \qquad (11\text{-}5)$$

where

$$\left[\frac{1}{2}\sum_{\alpha} \mu^{\mathrm{e}}_{\alpha\alpha} \hat{J}_{\alpha}{}^2\right] \Phi_{\mathrm{rot}}(\theta, \phi, \chi) = E_{\mathrm{rot}} \Phi_{\mathrm{rot}}(\theta, \phi, \chi) \qquad (11\text{-}6)$$

and

$$\frac{1}{2}(\hat{P}_r + \lambda_r Q_r{}^2) \Phi_{v_r}(Q_r) = E_{v_r} \Phi_{v_r}(Q_r). \qquad (11\text{-}7)$$

Equation (11-6) is the rigid rotor Schrödinger equation, and (11-7) is the harmonic oscillator Schrödinger equation.

11.2 THE RIGID ROTOR SCHRÖDINGER EQUATION

We will first determine the eigenfunctions and eigenvalues of the rigid rotor Schrödinger equation given in Eq. (11-6), and it is useful to consider three separate cases (linear molecules are discussed in Chapter 17):

(i) The symmetric top molecule, in which two of the $\mu^{\mathrm{e}}_{\alpha\alpha}$ are equal to each other,

(ii) The spherical top molecule, in which all three $\mu^{e}_{\alpha\alpha}$ are equal to each other, and

(iii) The asymmetric top molecule, in which all three $\mu^{e}_{\alpha\alpha}$ are different.

We write the rigid rotor Hamiltonian (in cm^{-1} units) in the principal axis system as

$$\hat{H}_{\rm rot} = \hbar^{-2}(A_{\rm e}\hat{J}_a{}^2 + B_{\rm e}\hat{J}_b{}^2 + C_{\rm e}\hat{J}_c{}^2), \tag{11-8}$$

where the rotational constants (in cm^{-1}) have been introduced and they are defined by

$$A_{\rm e} = \hbar^2\mu^{\rm e}_{aa}/(2hc), \qquad \text{etc.} \tag{11-9}$$

The principal inertial axes of the equilibrium configuration are labeled a, b, and c so that the rotational constants are in the order $A_{\rm e} \geq B_{\rm e} \geq C_{\rm e}$ (see the discussion given in connection with Fig. 10-2 on page 210).

11.2.1 The symmetric top molecule

From Section 10.3 we see that the operators $\boldsymbol{J}^2$, $\hat{J}_\zeta$, and $\hat{J}_z$ commute with each other. The simultaneous eigenfunctions of the three operators are straightforwardly determined to be the irreducible representation matrices (the so-called rotation matrices) of the rotation group $\boldsymbol{K}$ discussed in Chapter 7 [see, for example, Section 3-10 of Zare (1988)]. The eigenvalues of $\hat{\boldsymbol{J}}^2$ and $\hat{J}_\zeta$ are given in Eqs. (10-88)-(10-89) and the eigenvalue of $\hat{J}_z$ is $k\hbar$, where the molecule fixed projection quantum number k (like the space fixed projection quantum number m_J) runs over the $2J+1$ values from $-J$ to $+J$. Because of the form of the symmetric top Hamiltonian [see Eq. (11-11) below] it is easy to show that its eigenfunctions are these same rotation matrices (multiplied by a normalization constant). In Edition 1 we outlined the old fashioned way of determining the eigenfunctions by solving the symmetric top Schrödinger equation. There is no need to do that.

For a symmetric top molecule either $A_{\rm e} > B_{\rm e} = C_{\rm e}$ for a prolate symmetric top (such as CH_3F) or $A_{\rm e} = B_{\rm e} > C_{\rm e}$ for an oblate symmetric top (such as BF_3). The rigid rotor Schrödinger equation for a prolate top is

$$\hbar^{-2}[A_{\rm e}\hat{J}_a{}^2 + B_{\rm e}(\hat{J}_b{}^2 + \hat{J}_c{}^2)]\Phi_{\rm rot}(\theta,\phi,\chi) = E_{\rm rot}\Phi_{\rm rot}(\theta,\phi,\chi). \tag{11-10}$$

For a prolate top the a axis is chosen as the z axis ($\mathrm{I^r}$ convention) so that Eq. (11-10) becomes

$$\hbar^{-2}[B_{\rm e}\hat{\boldsymbol{J}}^2 + (A_{\rm e} - B_{\rm e})\hat{J}_z^2]\Phi_{\rm rot}(\theta,\phi,\chi) = E_{\rm rot}\Phi_{\rm rot}(\theta,\phi,\chi). \tag{11-11}$$

Using the eigenvalues and eigenfunctions of $\hat{\boldsymbol{J}}^2$ and $\hat{J}_z$ we obtain

$$E_{\rm rot} = B_{\rm e}J(J+1) + (A_{\rm e} - B_{\rm e})k^2, \tag{11-12}$$

and (making the appropriate normalization with the volume element for integration over the Euler angles being $d\tau = \sin\theta\, d\theta\, d\phi\, d\chi$)

$$\begin{aligned}\Phi_{\text{rot}}(\theta,\phi,\chi) = {} & [(2J+1)/(8\pi^2)]^{1/2}[D^{(J)}_{mk}(\phi,\theta,\chi)]^* \\ = {} & (-1)^{m-k}[(2J+1)/(8\pi^2)]^{1/2}[D^{(J)}_{-m-k}(\phi,\theta,\chi)]. \qquad (11\text{-}13)\end{aligned}$$

The three quantum numbers J, k, and m can have the values

$$J = 0,1,2,...; \quad k = 0,\pm1,\pm2,...\pm J; \quad \text{and} \quad m = 0,\pm1,\pm2,...,\pm J. \qquad (11\text{-}14)$$

The eigenfunctions depend on all three quantum numbers, but the energy only depends on the values of J and $K = |k|$. The function $D^{(J)}_{mk}(\phi,\theta,\chi)$ in Eq. (11-13) is the (m,k) element in the matrix representation $D^{(J)}$ of the group $\boldsymbol{K}$ for the rotation operation $[\phi,\theta,\chi]$ in the passive picture [see Eqs. (3.125), (3.54), and (3.57) in Zare (1988)].[1] Using this we have

$$\Phi_{\text{rot}}(\theta,\phi,\chi) = X_{Jkm}\, e^{im\phi}e^{ik\chi} \times \left\{\sum_\sigma (-1)^\sigma \frac{(\cos\frac{1}{2}\theta)^{2J+k-m-2\sigma}(-\sin\frac{1}{2}\theta)^{m-k+2\sigma}}{\sigma!(J-m-\sigma)!(m-k+\sigma)!(J+k-\sigma)!}\right\}, \qquad (11\text{-}15)$$

where

$$X_{Jkm} = [(J+m)!(J-m)!(J+k)!(J-k)!(2J+1)/(8\pi^2)]^{1/2};$$

the index σ in the sum runs from 0 or $(k-m)$, whichever is the larger, up to $(J-m)$ or $(J+k)$, whichever is the smaller. We can write the symmetric top wavefunction as

$$\Phi_{\text{rot}}(\theta,\phi,\chi) = [1/(2\pi)]^{1/2}S_{Jkm}(\theta,\phi)e^{ik\chi}, \qquad (11\text{-}16)$$

and we can relate the function $S_{Jkm}(\theta,\phi)$ to other standard functions as follows:

$$\begin{aligned}S_{J0m}(\theta,\phi) &= Y_{Jm}(\theta,\phi) \qquad (11\text{-}17)\\ &= [1/(2\pi)]^{1/2}\Theta_{Jm}(\theta)e^{im\phi}, \qquad (11\text{-}18)\end{aligned}$$

where $Y_{Jm}(\theta,\phi)$ is a spherical harmonic function and $\Theta_{Jm}(\theta)$ is a normalized associated Legendre polynomial [see Section 1.3 of Zare (1988)]. We see that

$$Y_{Jm}(\theta,\phi) = [(2J+1)/(4\pi)]^{1/2}[D^{(J)}_{m0}(\phi,\theta,0)]^*, \qquad (11\text{-}19)$$

where we have put $\chi = 0$ in the D function to make it explicitly clear that when $k = 0$ the D function does not depend on χ.

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[1] See also the remarks between Eqs. (7-43) and (7-44), and the Bibliographical Notes of Chapter 7 concerning the $\boldsymbol{K}$(spatial) group.

For an oblate rotor the rotational Schrödinger equation is

$$\hbar^{-2}[B_e(J_a{}^2 + J_b{}^2) + C_e J_c{}^2]\Phi_{\mathrm{rot}} = E_{\mathrm{rot}}\Phi_{\mathrm{rot}}. \tag{11-20}$$

Choosing the c axis as the z axis (a type $\mathrm{III}^{\mathrm{r}}$ convention) we obtain exactly the same wave equation as for the prolate rotor except that A_e is replaced by C_e. Thus for an oblate rotor (in cm^{-1})

$$E_{\mathrm{rot}} = B_e J(J+1) - (B_e - C_e)k^2, \tag{11-21}$$

and Φ_{rot} is as given in Eqs. (11-13)-(11-19).

11.2.2 The spherical top molecule

For a spherical top molecule $A_e = B_e = C_e$ and the rigid rotor Schrödinger equation is

$$\hbar^{-2} B_e \boldsymbol{J}^2 \Phi_{\mathrm{rot}} = E_{\mathrm{rot}}\Phi_{\mathrm{rot}}, \tag{11-22}$$

so that

$$E_{\mathrm{rot}} = B_e J(J+1), \tag{11-23}$$

and the wavefunctions are as for a symmetric top molecule given in Eq. (11-15).

The rigid rotor rotational eigenfunctions of all symmetric top and spherical top molecules are the same function [given in Eq. (11-15)] of the Euler angles θ, ϕ and χ, and we see that the function does not involve the rotational constants of the molecule; we call the wavefunction the ***symmetric top wavefunction*** and write it[2] $|J, k, m\rangle$.

11.2.3 The angular momentum ladder operators

Before discussing the asymmetric top it is useful to determine some angular momentum matrix elements in the symmetric top wavefunctions. To do this we will use angular momentum ***ladder operators***. They are introduced by the following problem.

Problem 11-1. Suppose $\hat{A}$ is an operator with eigenfunctions ψ_k and eigenvalues a_k, i.e.,

$$\hat{A}\psi_k = a_k\psi_k. \tag{11-24}$$

Suppose further that we find an operator, $\hat{O}$, say, that is such that its commutator with $\hat{A}$ is a constant multiple of itself, i.e.,

$$[\hat{A}, \hat{O}] = b\hat{O}, \tag{11-25}$$

---

[2] For electronic states having $S > 0$ the symmetric top wavefunction is denoted $|N, k, m\rangle$.

where b is a constant. Prove that in these circumstances $\hat{O}\psi_k$ is an eigenfunction of $\hat{A}$ with eigenvalue $(a_k + b)$, i.e., that

$$\hat{A}[\hat{O}\psi_k] = (a_k + b)[\hat{O}\psi_k]. \tag{11-26}$$

Answer. Starting with Eq. (11-25) and operating both sides on an eigenfunction ψ_k of $\hat{A}$ we have

$$\hat{A}\hat{O}\psi_k - \hat{O}\hat{A}\psi_k = b\hat{O}\psi_k, \tag{11-27}$$

i.e.,

$$\hat{A}[\hat{O}\psi_k] - \hat{O}a_k\psi_k = b[\hat{O}\psi_k]$$

and thus

$$\hat{A}[\hat{O}\psi_k] = a_k[\hat{O}\psi_k] + b[\hat{O}\psi_k],$$

from which Eq. (11-26) directly follows. If b is zero, i.e., if $\hat{A}$ and $\hat{O}$ commute, then $\hat{O}\psi_k$ and ψ_k are both eigenfunctions of $\hat{A}$ with the same eigenvalue.

An operator such as $\hat{O}$, which obeys Eq. (11-25) in Problem 11-1, is a *ladder operator* for the eigenfunctions of $\hat{A}$ since it changes each eigenfunction of $\hat{A}$ into a new eigenfunction in which the eigenvalue is laddered up or down as b is positive or negative. These operators are also called shift operators, step-up and step-down operators, or raising and lowering operators.

We introduce the angular momentum ladder operators as follows. From Eq. (10-92) we deduce that

$$[\hat{J}_z, (\hat{J}_x + i\hat{J}_y)] = -\hbar(\hat{J}_x + i\hat{J}_y) \tag{11-28}$$

and

$$[\hat{J}_z, (\hat{J}_x - i\hat{J}_y)] = +\hbar(\hat{J}_x - i\hat{J}_y). \tag{11-29}$$

Defining

$$\hat{J}_{\mathrm{m}}{}^{\pm} = (\hat{J}_x \pm i\hat{J}_y), \tag{11-30}$$

where m stands for molecule fixed, we see that $\hat{J}_{\mathrm{m}}{}^{+}$ and $\hat{J}_{\mathrm{m}}{}^{-}$ are ladder operators for the eigenfunctions of $\hat{J}_z$; $\hat{J}_{\mathrm{m}}{}^{+}$ ladders down by $\hbar$ and $\hat{J}_{\mathrm{m}}{}^{-}$ ladders up by $\hbar$, i.e., if

$$\hat{J}_z\Phi = k\hbar\Phi \tag{11-31}$$

then [unless $k = +J$ (or $-J$) when $\hat{J}_{\mathrm{m}}{}^{-}\Phi$ (or $\hat{J}_{\mathrm{m}}{}^{+}\Phi$) will vanish since $|k| \leq J$]

$$\hat{J}_z[\hat{J}_{\mathrm{m}}{}^{\pm}\Phi] = (k \mp 1)\hbar[\hat{J}_{\mathrm{m}}{}^{\pm}\Phi], \tag{11-32}$$

where the ± and ∓ signs are correlated. Since $\hat{J}_x$ and $\hat{J}_y$ commute with $\hat{J}^2$, the ladder operators $\hat{J}_m{}^+$ and $\hat{J}_m{}^-$ each commute with $\hat{\boldsymbol{J}}^2$ so that if

$$\hat{\boldsymbol{J}}^2\Phi = J(J+1)\hbar^2\Phi \tag{11-33}$$

then

$$\hat{\boldsymbol{J}}^2[\hat{J}_m{}^{\pm}\Phi] = J(J+1)\hbar^2[\hat{J}_m{}^{\pm}\Phi]. \tag{11-34}$$

Similarly the operators (where s stands for space fixed)

$$\hat{J}_s{}^{\pm} = (\hat{J}_\xi \pm i\hat{J}_\eta) \tag{11-35}$$

can be formed from the space fixed components of $\hat{\boldsymbol{J}}$, and from Eq. (10-90) we see that

$$[\hat{J}_\zeta, \hat{J}_s{}^{\pm}] = \pm\hbar\hat{J}_s{}^{\pm}. \tag{11-36}$$

Thus $\hat{J}_s{}^+$ and $\hat{J}_s{}^-$ are ladder operators for the eigenfunctions of $\hat{J}_\zeta$ and if

$$\hat{J}_\zeta\Phi = m\hbar\Phi, \tag{11-37}$$

then [unless $m = +J$ (or $-J$) when $\hat{J}_s{}^+\Phi$ (or $\hat{J}_s{}^-\Phi$) will vanish since $|m| \leq J$]

$$\hat{J}_\zeta[\hat{J}_s{}^{\pm}\Phi] = (m \pm 1)\hbar[\hat{J}_s{}^{\pm}\Phi]. \tag{11-38}$$

Note that there is a change in sign so that $\hat{J}_s{}^+$ ladders up whereas $\hat{J}_m{}^+$ ladders down (and vice versa for $\hat{J}_s{}^-$ and $\hat{J}_m{}^-$). This change in sign is a result of the different signs in the commutators for the molecule fixed and space fixed components of $\boldsymbol{J}$ [see Eqs. (10-92) and (10-90)].

The angular momentum ladder operators $\hat{J}_m{}^{\pm}$ and $\hat{J}_s{}^{\pm}$, in conjunction with the operators $\hat{\boldsymbol{J}}^2$, $\hat{J}_z$ and $\hat{J}_\zeta$, form a set of seven angular momentum operators that can be used to determine the symmetric top wavefunctions $|J,k,m\rangle$, and the matrix elements of the seven operators in the $|J,k,m\rangle$ basis. Since we have already written the symmetric top functions down in terms of the rotation matrices we will not present the full derivation here. However, we will present enough to obtain the nonvanishing matrix elements which we summarize in Table 11-1. The details are given in Section 1.2 in Zare (1988). We can write

$$|J,\pm|k|,\pm|m|\rangle = N_{\pm}'(\hat{J}_m{}^{\mp})^{|k|}(\hat{J}_s{}^{\pm})^{|m|}|J,0,0\rangle \tag{11-39}$$

and

$$|J,\mp|k|,\pm|m|\rangle = N_{\pm}''(\hat{J}_m{}^{\pm})^{|k|}(\hat{J}_s{}^{\pm})^{|m|}|J,0,0\rangle, \tag{11-40}$$

where $|J,0,0\rangle$ can be compactly written as

$$|J,0,0\rangle = \left\{\frac{[(2J+1)/(8\pi^2)]^{1/2}}{(2^J J!)}\right\}\frac{d^J}{(d\cos\theta)^J}(\cos^2\theta - 1)^J. \tag{11-41}$$

Equations (11-39) and (11-40) each represent two equations: one in which the upper ± (or ∓) signs are used and the other in which the lower signs are used. The normalization factors $N_{\pm}'$ and $N_{\pm}''$, which involve a phase factor, must be determined. To determine them we write

$$|J,k,m\pm 1\rangle = N_{\pm}\hat{J}_{s}{}^{\pm}|J,k,m\rangle, \tag{11-42}$$

where $|J,k,m\rangle$ is normalized and $N_{\pm}$ is required so that the function $|J,k,m\pm 1\rangle$ is normalized. Multiplying each side of Eq. (11-42) by its complex conjugate and integrating over $d\tau = \sin\theta\, d\theta\, d\phi\, d\chi$ we obtain

$$\langle J,k,m\pm 1|J,k,m\pm 1\rangle = |N_{\pm}|^{2}\langle J,k,m|(\hat{J}_{s}{}^{\mp}\hat{J}_{s}{}^{\pm})|J,k,m\rangle. \tag{11-43}$$

Now

$$\hat{J}_{s}{}^{\mp}\hat{J}_{s}{}^{\pm} = \hat{\boldsymbol{J}}^{2} - \hat{J}_{\zeta}(\hat{J}_{\zeta}\pm\hbar) \tag{11-44}$$

and

$$\langle J,k,m|[\hat{\boldsymbol{J}}^{2} - \hat{J}_{\zeta}(\hat{J}_{\zeta}\pm\hbar)]|J,k,m\rangle = [J(J+1) - m(m\pm 1)]\hbar^{2}. \tag{11-45}$$

We want $N_{\pm}$ to be such that the left hand side of Eq. (11-43) is unity; therefore

$$|N_{\pm}|^{2} = \frac{1}{\hbar^{2}[J(J+1) - m(m\pm 1)]} \tag{11-46}$$

and

$$N_{\pm} = \frac{e^{\pm i\delta}}{\hbar[J(J+1) - m(m\pm 1)]^{1/2}}, \tag{11-47}$$

where δ is an arbitrary phase factor.[3] By convention [Condon and Shortley (1953)] the choice $\delta = 0$ is made so that $N_{\pm}$ is real and positive, and we obtain

$$|J,k,m\pm 1\rangle = \frac{1}{\hbar[J(J+1) - m(m\pm 1)]^{1/2}}\hat{J}_{s}{}^{\pm}|J,k,m\rangle, \tag{11-48}$$

which leads to the result

$$\langle J,k,m\pm 1|\hat{J}_{s}{}^{\pm}|J,k,m\rangle = \hbar[J(J+1) - m(m\pm 1)]^{1/2}. \tag{11-49}$$

Using $\hat{J}_{\mathrm{m}}{}^{\pm}$, and a similar phase factor choice, we obtain

$$|J,k\mp 1,m\rangle = \frac{1}{\hbar[J(J+1) - k(k\mp 1)]^{1/2}}\hat{J}_{\mathrm{m}}{}^{\pm}|J,k,m\rangle, \tag{11-50}$$

so that

$$\langle J,k\mp 1,m|\hat{J}_{\mathrm{m}}{}^{\pm}|J,k,m\rangle = \hbar[J(J+1) - k(k\mp 1)]^{1/2}. \tag{11-51}$$

---

[3] There is an error in Eq. (2) of Section 3^{3} of Condon and Shortley (1953), but since the choice $\delta = 0$ is made it is of no consequence.

From these results we determine that $N_+' = N_+'' = N_-' = N_-'' = N$ say, where N is real and positive. We can write Eqs. (11-39) and (11-40) as

$$|J,(\pm)|k|,\pm|m|\rangle = N(\hat{J}_{\mathrm{m}}^{(\mp)})^{|k|}(\hat{J}_{\mathrm{s}}^{\pm})^{|m|}|J,0,0\rangle, \qquad (11\text{-}52)$$

where J, k, and m are integral and

$$N = \{(J-|m|)!(J-|k|)!/[(J+|m|)!(J+|k|)!]\}^{1/2}\hbar^{-(|k|+|m|)};$$

the $(\pm)$ and $(\mp)$ are correlated and the two $\pm$ are correlated so that Eq. (11-52) is four equations in all. The nonvanishing matrix elements of $\hat{\boldsymbol{J}}^2, \hat{J}_z, \hat{J}_\zeta, \hat{J}_{\mathrm{m}}^{\pm}$ [from Eq. (11-51)], and $\hat{J}_{\mathrm{s}}^{\pm}$ [from Eq. (11-49)] in the symmetric top wavefunctions $|J,k,m\rangle$ are collected together in Table 11-1.

Table 11-1

Nonvanishing matrix elements[a] of components of the rovibronic angular momentum $\hat{\boldsymbol{J}}$

$\langle J,k,m\|\hat{\boldsymbol{J}}^2\|J,k,m\rangle$	=	$J(J+1)\hbar^2$
$\langle J,k,m\|\hat{J}_z\|J,k,m\rangle$	=	$k\hbar$
$\langle J,k,m\|\hat{J}_\zeta\|J,k,m\rangle$	=	$m\hbar$
$\langle J,k,m\pm 1\|\hat{J}_{\mathrm{s}}^{\pm}\|J,k,m\rangle$	=	$\hbar[J(J+1)-m(m\pm 1)]^{1/2}$
$\langle J,k\mp 1,m\|\hat{J}_{\mathrm{m}}^{\pm}\|J,k,m\rangle$	=	$\hbar[J(J+1)-k(k\mp 1)]^{1/2}$

[a] In a basis of symmetric top wavefunctions, where $\hat{J}_{\mathrm{m}}^{\pm} = \hat{J}_x \pm i\hat{J}_y$ and $\hat{J}_{\mathrm{s}}^{\pm} = \hat{J}_\xi \pm i\hat{J}_\eta$.

11.2.4 The asymmetric top molecule

For an asymmetric top molecule the rigid rotor rotational Hamiltonian is [from Eq. (11-8)]

$$\hat{H}_{\mathrm{rot}} = \hbar^{-2}(A_{\mathrm{e}}\hat{J}_a^{\,2} + B_{\mathrm{e}}\hat{J}_b^{\,2} + C_{\mathrm{e}}\hat{J}_c^{\,2}). \qquad (11\text{-}53)$$

The expressions for $\hat{J}_a^{\,2}, \hat{J}_b^{\,2}$, and $\hat{J}_c^{\,2}$ in terms of the Euler angles depend on the convention used to identify the a, b, and c axes with the x, y and z axes in Fig. 10-1. Regardless of which convention is used the way we solve the rotational Schrödinger equation is to set up the Hamiltonian matrix in a basis of symmetric top wavefunctions and diagonalize it to obtain the energies and wavefunctions. The wavefunctions are obtained as a linear combination of symmetric top wavefunctions with coefficients that are functions of A_{e}, B_{e}, and C_{e}. We will demonstrate the technique using a type $\mathrm{I^r}$ convention and briefly discuss the results of using a type $\mathrm{III^r}$ convention at the end of the section.

In a type I^{r} convention the Hamiltonian for an asymmetric top is

$$\hat{H}_{\mathrm{rot}} = \hbar^{-2}(A_e\hat{J}_z{}^2 + B_e\hat{J}_x{}^2 + C_e\hat{J}_y{}^2). \tag{11-54}$$

We set up the Hamiltonian matrix in $|J,k,m\rangle$ symmetric top functions. To do this it is convenient to rewrite the Hamiltonian as

$$\begin{aligned}\hat{H}_{\mathrm{rot}} = \hbar^{-2}\{[(B_e + C_e)/2]\hat{\boldsymbol{J}}^2 &+ [A_e - (B_e + C_e)/2]\hat{J}_z{}^2 \\ &+ [(B_e - C_e)/4][(\hat{J}_{\mathrm{m}}{}^{+})^2 + (\hat{J}_{\mathrm{m}}{}^{-})^2]\}.\end{aligned} \tag{11-55}$$

We use a symmetric top basis set $|J,k,m\rangle$ with a type I^{r} convention and so the k quantum number refers to rotational angular momentum about the a axis. As a result in a type I^{r} convention we sometimes write the basis set as $|J,k_a,m\rangle$ where we introduce k_a as the a axis rotational quantum number. To determine matrix elements of the Hamiltonian we need the matrix elements of $\hat{\boldsymbol{J}}^2$, $\hat{J}_z{}^2$, $(\hat{J}_{\mathrm{m}}{}^{+})^2$, and $(\hat{J}_{\mathrm{m}}{}^{-})^2$. From the results in Table 11-1 the only non-vanishing matrix elements of the operators are

$$\langle J,k,m|\hat{\boldsymbol{J}}^2|J,k,m\rangle = J(J+1)\hbar^2, \tag{11-56}$$

$$\langle J,k,m|\hat{J}_z{}^2|J,k,m\rangle = k^2\hbar^2, \tag{11-57}$$

$$\begin{aligned}\langle J,k-2,m|(\hat{J}_{\mathrm{m}}{}^{+})^2|J,k,m\rangle = \{[J(J+1) &- (k-1)(k-2)][J(J+1) \\ &- k(k-1)]\}^{1/2}\hbar^2.\end{aligned} \tag{11-58}$$

and

$$\begin{aligned}\langle J,k+2,m|(\hat{J}_{\mathrm{m}}{}^{-})^2|J,k,m\rangle = \{[J(J+1) &- (k+1)(k+2)][J(J+1) \\ &- k(k+1)]\}^{1/2}\hbar^2,\end{aligned} \tag{11-59}$$

We see that $\hat{H}_{\mathrm{rot}}$ for an asymmetric top only has nonvanishing matrix elements between states of the same J and m and between states having the same k values or k values differing by two. As a result the Hamiltonian matrix factors into blocks, one for each J value, and each of the blocks consists of $2J+1$ identical blocks, one for each m value. In the absence of external fields the m degeneracy only affects intensities; we neglect it and focus attention only on $m=0$ states. Each ($m=0$) J block can be block diagonalized into four blocks by forming sum (+) and difference (−) combinations of $|J,K,0\rangle$ and $|J,-K,0\rangle$ functions where $K=|k|$. This is because $\hat{H}_{\mathrm{rot}}$ has no matrix elements between k-even and k-odd functions or between + and − functions.[4] The four blocks are called E^+, E^-, O^+, and O^- depending on whether k is even or odd, and on whether they are + or − functions. The solution to the next problem will demonstrate this point. A general result for the asymmetric top Hamiltonian matrix of a given J is that for J even the E^+ block has dimension $(J+2)/2$ and the other three blocks have dimension $J/2$, whereas for J odd the E^- block has dimension $(J-1)/2$ and the other three blocks have dimension $(J+1)/2$.

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[4] This block diagonalization of the asymmetric rotor Hamiltonian matrix occurs because of symmetry in the molecular rotation group [see Table 12-16].

Problem 11-2. Determine the rigid rotor energies and wavefunctions for an asymmetric top molecule with rotational constants A_e, B_e, and C_e for the states with $J = 0, 1$, and 2.

Answer. We consider $J = 0, 1$, and 2 separately and for each J block of the Hamiltonian matrix we neglect the m degeneracy and suppress the m label so that we label the basis functions $|J, k\rangle$.

The $J = 0$ block of the Hamiltonian matrix is a 1×1 block involving the $J = k = 0$ basis set wavefunction. This matrix element is zero and so $E_{\rm rot}(J = 0) = 0$ and $\Phi_{\rm rot}(J = 0) = (8\pi^2)^{-1/2}$.

The $J = 1$ block is a 3×3 block involving $|J, k\rangle$ functions with $k = -1, 0$, and $+1$; i.e., $|1, -1\rangle, |1, 0\rangle$, and $|1, +1\rangle$. We form sum and difference combinations and we label them $|J, K, A^{\pm}\rangle$ where $A = O$ or E (for odd or even)

$$|1, 1, O^+\rangle = [|1, +1\rangle + |1, -1\rangle]/\sqrt{2}, \tag{11-60}$$

$$|1, 1, O^-\rangle = [|1, +1\rangle - |1, -1\rangle]/\sqrt{2}, \tag{11-61}$$

and

$$|1, 0, E^+\rangle = |1, 0\rangle. \tag{11-62}$$

These functions are O^+, O^-, and E^+ type functions, respectively, and $\hat{H}_{\rm rot}$ has no off-diagonal matrix elements between them [the reader can test this by using the results in Eqs. (11-56)-(11-59)]. Thus these are eigenfunctions of $\hat{H}_{\rm rot}$ and the eigenvalues are given by the diagonal matrix elements of $\hat{H}_{\rm rot}$ in these functions. For the O^+ level the energy, using the notation $E_{\rm rot}(J, A^{\pm})$, is given by

$$E_{\rm rot}(1, O^+) = \frac{1}{2}[\langle 1, +1| + \langle 1, -1|]\hat{H}_{\rm rot}[|1, +1\rangle + |1, -1\rangle]. \tag{11-63}$$

From Eqs. (11-56) and (11-57) with Eq. (11-55) we see that

$$\begin{aligned}\langle 1, -1|\hat{H}_{\rm rot}|1, -1\rangle &= \langle 1, +1|\hat{H}_{\rm rot}|1, +1\rangle \\ &= [(B_e + C_e)/2]2 + [A_e - (B_e + C_e)/2] \\ &= A_e + (B_e + C_e)/2,\end{aligned} \tag{11-64}$$

and from Eqs. (11-58) and (11-59) with Eq. (11-55) we have

$$\langle 1, -1|\hat{H}_{\rm rot}|1, +1\rangle = \langle 1, +1|\hat{H}_{\rm rot}|1, -1\rangle = [(B_e - C_e)/4]2 = (B_e - C_e)/2. \tag{11-65}$$

Substituting Eqs. (11-64) and (11-65) into Eq. (11-63) we obtain

$$E_{\rm rot}(1, O^+) = A_e + B_e. \tag{11-66}$$

It is straightforward to determine in a similar manner that

$$E_{\rm rot}(1, O^-) = A_e + C_e \tag{11-67}$$

and

$$E_{\mathrm{rot}}(1, E^{+}) = B_{\mathrm{e}} + C_{\mathrm{e}}. \tag{11-68}$$

For $J = 2$ the appropriate basis functions are

$$|2, 2, E^{+}\rangle = [|2, +2\rangle + |2, -2\rangle]\sqrt{2}, \tag{11-69}$$

$$|2, 2, E^{-}\rangle = [|2, +2\rangle - |2, -2\rangle]\sqrt{2}, \tag{11-70}$$

$$|2, 1, O^{+}\rangle = [|2, +1\rangle + |2, -1\rangle]\sqrt{2}, \tag{11-71}$$

$$|2, 1, O^{-}\rangle = [|2, +1\rangle - |2, -1\rangle]\sqrt{2}, \tag{11-72}$$

and

$$|2, 0, E^{+}\rangle = |2, 0\rangle. \tag{11-73}$$

The only nonvanishing off-diagonal matrix element of $\hat{H}_{\mathrm{rot}}$ between the five functions is that between the two E^{+} functions. From the three 1×1 blocks we obtain energies $E_{\mathrm{rot}}(J, A^{\pm})$ given by

$$E_{\mathrm{rot}}(2, E^{-}) = 4A_{\mathrm{e}} + B_{\mathrm{e}} + C_{\mathrm{e}}, \tag{11-74}$$

$$E_{\mathrm{rot}}(2, O^{+}) = A_{\mathrm{e}} + 4B_{\mathrm{e}} + C_{\mathrm{e}}, \tag{11-75}$$

and

$$E_{\mathrm{rot}}(2, O^{-}) = A_{\mathrm{e}} + B_{\mathrm{e}} + 4C_{\mathrm{e}}, \tag{11-76}$$

The 2×2 block of $\hat{H}_{\mathrm{rot}}$ for the $J = 2$ E^{+} functions is

	$\|2, 0, E^{+}\rangle$	$\|2, 2, E^{+}\rangle$
$\langle 2, 0, E^{+}\|$	$3(B_{\mathrm{e}} + C_{\mathrm{e}})$	$\sqrt{3}(B_{\mathrm{e}} - C_{\mathrm{e}})$
$\langle 2, 2, E^{+}\|$	$\sqrt{3}(B_{\mathrm{e}} - C_{\mathrm{e}})$	$4A_{\mathrm{e}} + B_{\mathrm{e}} + C_{\mathrm{e}}$

The eigenvalues of the matrix are

$$E^{\pm}_{\mathrm{rot}}(2, E^{+}) = 2(A_{\mathrm{e}} + B_{\mathrm{e}} + C_{\mathrm{e}}) \pm [3(B_{\mathrm{e}} - C_{\mathrm{e}})^2 + (2A_{\mathrm{e}} - B_{\mathrm{e}} - C_{\mathrm{e}})^2]^{1/2} \tag{11-77}$$

and the eigenfunctions $\Phi^{\pm}_{\mathrm{rot}}(J, E^{+})$ are

$$\Phi^{-}_{\mathrm{rot}}(2, E^{+}) = [c^{+}|2, 0, E^{+}\rangle - c^{-}|2, 2, E^{+}\rangle]/\sqrt{2}, \tag{11-78}$$

and

$$\Phi^{+}_{\mathrm{rot}}(2, E^{+}) = [c^{-}|2, 0, E^{+}\rangle + c^{+}|2, 2, E^{+}\rangle]/\sqrt{2}, \tag{11-79}$$

where

$$c^{\pm} = \{1 \pm (2A_e - B_e - C_e)/[3(B_e - C_e)^2 + (2A_e - B_e - C_e)^2]^{1/2}\}^{1/2}. \tag{11-80}$$

The two functions are a mixture of $K = 0$ and $K = 2$ functions with coefficients depending on the rotational constants. As a result the functions are not eigenfunctions of $\hat{J}_z$ and we say that K (i.e., K_a) is not a *good* quantum number for them. The idea of a good quantum number will be discussed further in Section 13.1.2.

In the above discussion of the asymmetric top wavefunctions and energy levels a $\mathrm{I^r}$ convention was used and consequently the basis set consisted of $|J, k_a, m\rangle$ symmetric top functions. It is of interest to consider briefly what happens when we use a $\mathrm{III^r}$ convention and $|J, k_c, m\rangle$ basis functions. In a $\mathrm{III^r}$ convention the rigid rotor Hamiltonian becomes

$$\hat{H}_{\mathrm{rot}} = \hbar^{-2}(A_e\hat{J}_x{}^2 + B_e\hat{J}_y{}^2 + C_e\hat{J}_z{}^2), \tag{11-81}$$

which can be rewritten as

$$\hbar^{-2}\{[(A_e + B_e)/2]\hat{\boldsymbol{J}}^2 + [C_e - (A_e + B_e)/2]\hat{J}_z{}^2 + [(A_e - B_e)/4][(\hat{J}_m{}^{+})^2 + (\hat{J}_m{}^{-})^2]\}. \tag{11-82}$$

We set up the matrix of this Hamiltonian in a $|J, k, m\rangle = |J, k_c, m\rangle$ basis and diagonalize to get the energies and wavefunctions. The energies will be the same as obtained in the $\mathrm{I^r}$ basis but the wavefunctions will look different since the Euler angles are defined differently; also the $E^{\pm}$ and $O^{\pm}$ designations are different since K_c rather than K_a is used. In a $\mathrm{I^r}$ basis the Euler angles $\theta(\mathrm{I^r})$ and $\phi(\mathrm{I^r})$ are the polar angles of the a axis in the (ξ, η, ζ) axis system, and $\chi(\mathrm{I^r})$ is the angle between the c axis and the line of intersection of the bc and $\xi\eta$ planes. In a $\mathrm{III^r}$ basis the angles $\theta(\mathrm{III^r})$ and $\phi(\mathrm{III^r})$ are the polar angles of the c axis in the (ξ, η, ζ) axis system, and $\chi(\mathrm{III^r})$ is the angle between the b axis and the line of intersection of the ab and $\xi\eta$ planes. The relationship between the two sets of Euler angles is complicated; for example,

$$\theta(\mathrm{I^r}) = \arccos[-\sin\theta(\mathrm{III^r})\cos\chi(\mathrm{III^r})]. \tag{11-83}$$

Using relationships such as this it is possible to show that the asymmetric top wavefunctions obtained in the $\mathrm{I^r}$ basis are identical to those obtained in the $\mathrm{III^r}$ basis for a given molecule.

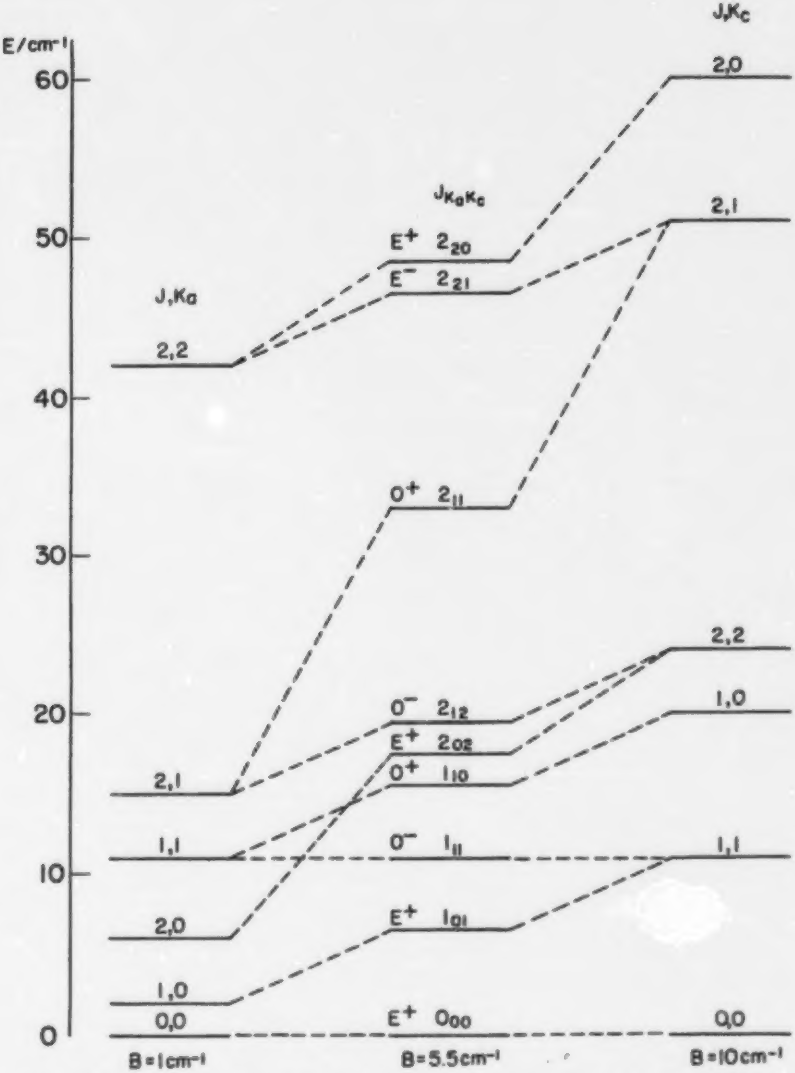
E/cm⁻¹
60
50
40
30
20
10
0
J,Ka
2,2
2,1
1,1
2,0
1,0
0,0
J_{KaKc}
E⁺ 2₂₀
E⁻ 2₂₁
O⁺ 2₁₁
O⁻ 2₁₂
E⁺ 2₀₂
O⁺ 1₁₀
O⁻ 1₁₁
E⁺ 1₀₁
E⁺ 0₀₀
J,Kc
2,0
2,1
2,2
1,0
1,1
0,0
B=1cm⁻¹
B=5.5cm⁻¹
B=10cm⁻¹

Fig. 11-1. The correlation of the $J = 0, 1$, and 2 energy levels of a rigid asymmetric top molecule having $A = 10$ cm^{-1}, $B = 5.5$ cm^{-1}, and $C = 1$ cm^{-1} (i.e., $\kappa = 0$) with those for the prolate top having $(A, B, C) = (10, 1, 1)$ cm^{-1} on the left, and with those for the oblate top having $(A, B, C) = (10, 10, 1)$ cm^{-1} on the right. The $E^{\pm}$ and $O^{\pm}$ designations depend on whether K_a is even (E) or odd (O), and on whether sum or difference functions $(|J, K_a\rangle \pm |J, -K_a\rangle)/\sqrt{2}$ occur in the basis set for the level considered.

If the asymmetric top molecule under study is a near prolate top, i.e., $B_e \approx C_e$, then in a type I^r basis the off-diagonal matrix elements will be small. If the molecule under study is a near oblate top; i.e., $A_e \approx B_e$, then in a III^r basis the off-diagonal matrix elements will be small. The degree of asymmetry in an asymmetric top is conveniently given by the value of

$$\kappa = (2B_e - A_e - C_e)/(A_e - C_e). \tag{11-84}$$

For a prolate top $\kappa = -1$, for an oblate top $\kappa = +1$, and for an asymmetric top $-1 < \kappa < +1$, with $\kappa = 0$ being the "most" asymmetric when B_e is halfway between A_e and C_e.

In Fig. 11-1 we show the correlation of the $J = 0, 1$, and 2 energy levels of a $\kappa = 0$ asymmetric top molecule with the $\kappa = \pm 1$ symmetric top limits. The $E^{\pm}$ and $O^{\pm}$ designations of the levels are shown for the asymmetric rotor levels in the I^r basis. It is customary to label the asymmetric top levels $J_{K_a K_c}$ where the labels K_a and K_c indicate the prolate and oblate levels respectively with which the level correlates ($K_a = |k_a|$ and $K_c = |k_c|$). These labels are very useful and we will also often refer to an asymmetric rotor level as being ee, eo, oe, or oo depending on whether K_a and K_c are even (e) or odd (o), respectively; e.g., the level 2_{21} is an eo level. The asymmetric top wavefunctions are not in general eigenfunctions of $\hat{J}_a$ or $\hat{J}_c$ and neither K_a or K_c is a good quantum number.

11.3 THE HARMONIC OSCILLATOR SCHRÖDINGER EQUATION

Before looking at the solution of the harmonic oscillator Schrödinger equation the following problem should be worked. We will use the answer in setting up the harmonic oscillator ladder operators.

Problem 11-3. In the harmonic oscillator equation the normal coordinate Q and its conjugate momentum $\hat{P} = -i\hbar\partial/\partial Q$ occur. Determine the values of the commutators $[\hat{P}^2, Q]$ and $[Q^2, \hat{P}]$.

Answer. Straightforward commutator manipulation gives

$$[\hat{P}^2, Q] = \hat{P}[\hat{P}, Q] + [\hat{P}, Q]\hat{P} = \hat{P}(-i\hbar) + (-i\hbar)\hat{P} = -2i\hbar\hat{P} \tag{11-85}$$

and

$$[Q^2, \hat{P}] = Q[Q, \hat{P}] + [Q, \hat{P}]Q = Q(i\hbar) + (i\hbar)Q = 2i\hbar Q. \tag{11-86}$$

Equations (11-85) and (11-86) are examples of the general relation

$$[\hat{A}\,\hat{B}, \hat{C}] = \hat{A}\,[\hat{B}, \hat{C}] + [\hat{A}\,, \hat{C}]\hat{B}, \tag{11-87}$$

where $\hat{A}$, $\hat{B}$, and $\hat{C}$ are arbitrary operators.

11.3.1 The one-dimensional harmonic oscillator

The one-dimensional harmonic oscillator wave equation can be written as

$$\hat{H}_{\text{ho}}\Phi_v = \frac{1}{2}(\hat{P}^2 + \lambda Q^2)\Phi_v = E_v\Phi_v. \tag{11-88}$$

To determine the eigenfunctions and eigenvalues of this Hamiltonian we introduce the operators

$$\hat{R}^+ = (1/\sqrt{2})(\hat{P} + i\lambda^{1/2}Q) \tag{11-89}$$

and

$$\hat{R}^- = (1/\sqrt{2})(\hat{P} - i\lambda^{1/2}Q) \tag{11-90}$$

The commutators of these with the harmonic oscillator Hamiltonian are [using Eqs. (11-85) and (11-86)]

$$[\hat{H}_{\text{ho}}, \hat{R}^+] = [1/(2\sqrt{2})](i\lambda^{1/2}[\hat{P}^2, Q] + \lambda[Q^2, \hat{P}]) = \hbar\lambda^{1/2}\hat{R}^+ \tag{11-91}$$

and

$$[\hat{H}_{\text{ho}}, \hat{R}^-] = -\hbar\lambda^{1/2}\hat{R}^-. \tag{11-92}$$

Thus from Eqs. (11-25) and (11-26) in Problem 11-1 we see that $\hat{R}^+$ is a "ladder up" operator and $\hat{R}^-$ is a "ladder down" operator so that if

$$\hat{H}_{\text{ho}}\Phi_v = E_v\Phi_v \tag{11-93}$$

then

$$\hat{H}_{\text{ho}}[\hat{R}^\pm\Phi_v] = (E_v \pm \hbar\lambda^{1/2})[\hat{R}^\pm\Phi_v]. \tag{11-94}$$

It is easy to see that

$$\hat{H}_{\text{ho}} = \hat{R}^+\hat{R}^- + \frac{1}{2}\hbar\lambda^{1/2} \tag{11-95}$$

and

$$\hat{H}_{\text{ho}} = \hat{R}^-\hat{R}^+ - \frac{1}{2}\hbar\lambda^{1/2}. \tag{11-96}$$

Thus, for example, eigenfunctions of $\hat{R}^+\hat{R}^-$ are eigenfunctions of $\hat{H}_{\text{ho}}$ and vice versa. If Φ_v is a normalized eigenfunction of $\hat{R}^+\hat{R}^-$ with eigenvalue a we have

$$a = \int \Phi_v^*(\hat{R}^+\hat{R}^-)\Phi_v dQ. \tag{11-97}$$

This equation can be rewritten as

$$a = \int (\hat{R}^- \Phi_v)^* (\hat{R}^- \Phi_v) dQ \tag{11-98}$$

$$= \int |\hat{R}^- \Phi_v|^2 dQ \tag{11-99}$$

and hence a (an eigenvalue of $\hat{R}^+ \hat{R}^-$) must be real and nonnegative. Since by definition $\lambda^{1/2}$ is real and positive the eigenvalues of $\hat{H}_{\text{ho}}$ must be real and nonnegative as a result of Eqs. (11-95) and (11-99). Since the eigenvalues of $\hat{H}_{\text{ho}}$ are real and nonnegative there must be a lowest one which we call E_0. We call the eigenfunction having this eigenvalue Φ_0. Applying $\hat{R}^-$ to Φ_0 must give zero since there is no eigenfunction having a lower eigenvalue. Thus we can write

$$\hat{R}^- \Phi_0 = [(-i\hbar/\sqrt{2})\partial/\partial Q - i(\lambda/2)^{1/2} Q]\Phi_0 = 0, \tag{11-100}$$

which is a first order differential equation for Φ_0 that yields as solution the normalized function

$$\Phi_0 = (2\lambda^{1/2}/h)^{1/4} \exp[-(\lambda^{1/2}/2\hbar)Q^2], \tag{11-101}$$

where a real and positive phase factor choice has been made. Applying $\hat{R}^+$ to Eq. (11-100) we obtain

$$\hat{R}^+ \hat{R}^- \Phi_0 = 0, \tag{11-102}$$

and from Eq. (11-95) we see that we can rewrite Eq. (11-102) as

$$(\hat{H}_{\text{ho}} - \hbar\lambda^{1/2}/2)\Phi_0 = 0, \tag{11-103}$$

i.e.,

$$E_0 = \hbar\lambda^{1/2}/2. \tag{11-104}$$

We have thus determined the lowest eigenvalue E_0 and associated eigenfunction Φ_0 of the harmonic oscillator Hamiltonian.

The higher eigenvalues E_v and eigenfunctions Φ_v (where $v = 1, 2, 3, \ldots$) are obtained by operating with $(\hat{R}^+)^v$ on Φ_0. Clearly from the fact that $\hat{R}^+$ ladders up by $\hbar\lambda^{1/2}$ we must have

$$E_v = E_0 + v(\hbar\lambda^{1/2}) = \left(v + \frac{1}{2}\right) \hbar\lambda^{1/2}. \tag{11-105}$$

The constant λ is not always used and other constants defined from it are given by

$$\lambda^{1/2} = \omega = \hbar\gamma = 2\pi c\omega_e = 2\pi\nu, \tag{11-106}$$

where the units of $\lambda, \omega, \gamma, \omega_e$, and ν are $\sec^{-2}$, radians $\sec^{-1}$, $\text{erg}^{-1}\sec^{-2}$, cm^{-1}, and cycles $\sec^{-1}$ (Hz), respectively. The quantity ω_e is referred to as the ***harmonic vibrational wavenumber***. In the same manner as Eqs. (11-39) and (11-40) we can write

$$\Phi_v = N_v'(R^+)^v\Phi_0, \tag{11-107}$$

where $N_v{}'$ ensures normalization of Φ_v and it involves a phase factor. To follow arguments very similar to those used in Eqs. (11-42)-(11-47) we write

$$\Phi_{v\pm 1} = N_\pm R^\pm \Phi_v, \tag{11-108}$$

where Φ_v is normalized and $N_\pm$ is required for $\Phi_{v\pm 1}$ to be normalized. Multiplying each side on the left by its complex conjugate and integrating, and noting that [from Eqs. (11-95) and (11-96) and using $\hbar^2\gamma = \hbar\lambda^{1/2}$]

$$\langle\Phi_v|R^- R^+|\Phi_v\rangle = (v+1)\hbar^2\gamma \tag{11-109}$$

and that

$$\langle\Phi_v|R^+ R^-|\Phi_v\rangle = v\hbar^2\gamma, \tag{11-110}$$

we determine that

$$N_\pm = e^{\pm i\delta}\left[\left(v + \frac{1}{2} \pm \frac{1}{2}\right)\hbar^2\gamma\right]^{-1/2}. \tag{11-111}$$

It is conventional to choose the phase factor δ so that

$$e^{\pm i\delta} = \mp i, \tag{11-112}$$

and we obtain

$$N_\pm = \mp i\left[\left(v + \frac{1}{2} \pm \frac{1}{2}\right)\hbar^2\gamma\right]^{-1/2}. \tag{11-113}$$

For example, for $v = 1$ we have

$$\Phi_1 = [-i/(\hbar^2\gamma)^{1/2}]R^+\Phi_0 \tag{11-114}$$

$$= (\gamma/4\pi)^{1/4}(2\gamma^{1/2}Q)\exp(-\gamma Q^2/2). \tag{11-115}$$

In general we can write

$$\Phi_v = N_v H_v(\gamma^{1/2}Q)\exp(-\gamma Q^2/2), \tag{11-116}$$

where

$$N_v = \gamma^{1/4}/(\pi^{1/2}2^v v!)^{1/2} \tag{11-117}$$

and $H_v(\gamma^{1/2}Q)$ is a Hermite polynomial for which the first four values are [see Appendix III of Wilson, Decius, and Cross (1955)]

$$H_0(\gamma^{1/2}Q) = 1, \tag{11-118}$$

$$H_1(\gamma^{1/2}Q) = 2\gamma^{1/2}Q, \tag{11-119}$$

$$H_2(\gamma^{1/2}Q) = 4\gamma Q^2 - 2, \tag{11-120}$$

and

$$H_3(\gamma^{1/2}Q) = 8\gamma^{3/2}Q^3 - 12\gamma^{1/2}Q. \tag{11-121}$$

In general $H_v(\gamma^{1/2}Q)$ contains $(\gamma^{1/2}Q)$ to the powers $v, v-2, v-4, \ldots, 1$ or 0, i.e., either all even powers or all odd powers as v is even or odd, respectively.

Matrix elements that are particularly useful when working with harmonic oscillator functions are those of P and Q. From Eqs. (11-108) and (11-113) we can write

$$\langle\Phi_{v\pm1}|R^{\pm}|\Phi_v\rangle = \pm i\left[\left(v+\frac{1}{2}\pm\frac{1}{2}\right)\hbar^2\gamma\right]^{1/2}, \tag{11-122}$$

and these are the only nonvanishing matrix elements of the operators R^+ and R^-. From Eqs. (11-89) and (11-90) we see that

$$P = (R^+ + R^-)/\sqrt{2}, \tag{11-123}$$

and

$$Q = (R^+ - R^-)/(i\hbar\gamma\sqrt{2}), \tag{11-124}$$

so that the nonvanishing matrix elements of P and Q can be deduced from Eq. (11-122); they are given in Table 11-2. The phase factor choice given in Eq. (11-112) has resulted in the matrix elements of Q being real and those of P being imaginary. We see that the only nonvanishing matrix elements of P or Q have v values differing by ±1. Matrix elements of P^rQ^s where r and s are integers can be evaluated from the results in Table 11-2 (see Problem 11-3); the nonvanishing matrix elements $\langle v'|P^rQ^s|v''\rangle$ are those for which[5]

$$v' = v'' + r + s, v'' + r + s - 2, v'' + r + s - 4, \ldots, v'' - r - s. \tag{11-125}$$

---

[5] The lower limit is 0 or 1 if $v'' < (r + s)$.

Table 11-2

Nonvanishing matrix elements of normal coordinate Q and momentum $\dot{P}$ for the one-dimensional harmonic oscillator[a]

$\langle v+1\|Q\|v\rangle = \sqrt{(v+1)/(2\gamma)}$	$\langle v+1\|\dot{P}\|v\rangle = i\hbar\sqrt{(v+1)\gamma/2}$
$\langle v-1\|Q\|v\rangle = \sqrt{v/(2\gamma)}$	$\langle v-1\|\dot{P}\|v\rangle = -i\hbar\sqrt{v\gamma/2}$

[a] $\dot{P} = -i\hbar\partial/\partial Q$ and the one-dimensional harmonic oscillator functions $\Phi_v = |v\rangle$. We use $\gamma = \lambda^{1/2}/\hbar$ where the one-dimensional harmonic oscillator Hamiltonian is $\hat{H}_{\text{ho}} = \frac{1}{2}(\dot{P}^2 + \lambda Q^2)$. Equations (11-108) and (11-113) define the phase factor choice.

Problem 11-4. Determine the matrix element $\langle\Phi_4|\dot{P}Q^2|\Phi_3\rangle$ for the harmonic oscillator basis functions Φ_3 and Φ_4 (with $v = 3$ and 4, respectively) from the results in Table 11-2.

Answer. We can write the matrix element as follows:

$$\langle\Phi_4|\dot{P}Q^2|\Phi_3\rangle = \sum_{v,v'}\langle\Phi_4|\dot{P}|\Phi_v\rangle\langle\Phi_v|Q|\Phi_{v'}\rangle\langle\Phi_{v'}|Q|\Phi_3\rangle, \tag{11-126}$$

where we have used the law of matrix multiplication [see Eq. (5-3)]. Nonvanishing matrix elements of P and Q have $\Delta v = \pm 1$ so that there are only three nonvanishing terms in this sum and

$$\begin{aligned}\langle\Phi_4|\dot{P}Q^2|\Phi_3\rangle &= \langle\Phi_4|P|\Phi_5\rangle\langle\Phi_5|Q|\Phi_4\rangle\langle\Phi_4|Q|\Phi_3\rangle\\ &\quad + \langle\Phi_4|P|\Phi_3\rangle\langle\Phi_3|Q|\Phi_4\rangle\langle\Phi_4|Q|\Phi_3\rangle\\ &\quad + \langle\Phi_4|P|\Phi_3\rangle\langle\Phi_3|Q|\Phi_2\rangle\langle\Phi_2|Q|\Phi_3\rangle\\ &= [(-i\hbar\sqrt{5\gamma/2})\sqrt{5/2\gamma}\sqrt{4/2\gamma}] + [(i\hbar\sqrt{4\gamma/2})\sqrt{4/2\gamma}\sqrt{4/2\gamma}]\\ &\quad + [(i\hbar\sqrt{4\gamma/2}\sqrt{3/2\gamma}\sqrt{3/2\gamma}]\\ &= i\hbar(2/\gamma)^{1/2}.\end{aligned} \tag{11-127}$$

The harmonic oscillator Hamiltonian for a molecule is

$$\frac{1}{2}\sum_r(P_r^2 + \lambda_r Q_r^2) \tag{11-128}$$

from Eq. (11-1a). From the results of this section we see that the eigenfunctions of the Hamiltonian can be written

$$\begin{aligned}\Phi_{\text{vib}} &= \Phi_{v_1}(Q_1)\Phi_{v_2}(Q_2)\cdots\Phi_{v_{3N-6}}(Q_{3N-6})\\ &= \exp\left[-\frac{1}{2}\sum_r\gamma_r{Q_r}^2\right]\prod_r N_{v_r}H_{v_r}({\gamma_r}^{1/2}Q_r)\end{aligned} \tag{11-129}$$

and the eigenvalues are

$$E_{\mathrm{vib}} = \sum_r \left(v_r + \frac{1}{2}\right) \hbar^2 \gamma_r, \qquad (11\text{-}130)$$

where $\gamma_r = \lambda_r^{1/2}/\hbar$.

11.3.2 The two-dimensional isotropic harmonic oscillator

If the normal coordinate representation of a molecule contains a doubly degenerate irreducible representation then the degenerate pair of normal coordinates, Q_a and Q_b say, must have the same values for λ_a and λ_b, as we now show. Since (Q_a, Q_b) form the basis for a degenerate representation they must be "mixed" by at least one operation, R, say, of the symmetry group of the molecule, i.e.,

$$RQ_a = c_{aa}Q_a + c_{ab}Q_b \qquad (11\text{-}131)$$

and

$$RQ_b = c_{ba}Q_a + c_{bb}Q_b, \qquad (11\text{-}132)$$

where $c_{\alpha\beta}$ are transformation coefficients and the matrix of the $c_{\alpha\beta}$ is the unitary matrix representing R in the irreducible representation generated by Q_a and Q_b [i.e., $R(Q_a{}^2+Q_b{}^2) = (Q_a{}^2+Q_b{}^2)$]. However, since R is a symmetry operation it commutes with the Hamiltonian and the following operator equation must be true

$$R\hat{H}_{\mathrm{tdho}} = \hat{H}_{\mathrm{tdho}}R, \qquad (11\text{-}133)$$

where tdho stands for two-dimensional harmonic oscillator, but

$$\begin{aligned} R\hat{H}_{\mathrm{tdho}} &= R[\tfrac{1}{2}(\hat{P}_a{}^2 + \hat{P}_b{}^2 + \lambda_a Q_a{}^2 + \lambda_b Q_b{}^2)] \\ &= \{\tfrac{1}{2}[\hat{P}_a{}^2 + \hat{P}_b{}^2 + \lambda_a(c_{aa}^2 Q_a{}^2 + 2c_{aa}c_{ab}Q_aQ_b + c_{ab}^2 Q_b{}^2) \\ &\quad + \lambda_b(c_{ba}^2 Q_a{}^2 + 2c_{ba}c_{bb}Q_aQ_b + c_{bb}^2 Q_b{}^2)]\}R, \end{aligned} \qquad (11\text{-}134)$$

and the only way that the right hand sides of Eqs. (11-133) and (11-134) can be equal is if either

$$c_{ab} = c_{ba} = 0 \qquad (11\text{-}135)$$

or

$$\lambda_a = \lambda_b. \qquad (11\text{-}136)$$

This means that either [from Eq. (11-135)] Q_a and Q_b are not mixed by any symmetry operations if $\lambda_a \neq \lambda_b$, or if they are mixed then [from Eq. (11-136)] they must have the same frequency. In other words if $\lambda_a \neq \lambda_b$ then Q_a and Q_b cannot be the basis for a doubly degenerate irreducible representation of a symmetry group of the Hamiltonian, but if Q_a and Q_b are the basis for such a representation then it is necessary that $\lambda_a = \lambda_b$.

As a result of the above argument [see Eq. (11-135)] the normal coordinates Q_r that have nondegenerate λ_r will form the basis for one-dimensional (and hence irreducible) representations of a symmetry group of the Hamiltonian. A set of l normal coordinates $Q_{s1}, Q_{s2}, \ldots, Q_{sl}$ that all have the same normal frequency λ_s will form the basis for an l-dimensional representation of the group. This l-dimensional representation can be reducible or irreducible. If the representation is reducible then it is an accident requiring a fortuitous relationship to occur between the force constants and the nuclear masses; this is rare. Even if an accidental degeneracy occurs it is still possible to construct normal coordinates that transform irreducibly.

From Eq. (11-130) the energy of a pair of degenerate vibrations described by the normal coordinates Q_a and Q_b is given by

$$E(v_a, v_b) = \left[\left(v_a + \frac{1}{2}\right) + \left(v_b + \frac{1}{2}\right)\right] \hbar^2\gamma, \tag{11-137}$$

where $\hbar\gamma = \lambda_a^{1/2} = \lambda_b^{1/2}$, and there are systematic degeneracies, i.e.,

$$E(1,0) = E(1,0) = 2\hbar^2\gamma,$$

$$E(2,0) = E(1,1) = E(0,2) = 3\hbar^2\gamma, \quad \text{etc.} \tag{11-138}$$

Thus the energy of a level depends only on $(v_a + v_b)$ and each level has a degeneracy of $(v_a + v_b + 1)$. The wavefunction for this pair of vibrations is [from Eq. (11-129)] given by

$$\Phi_{v_a v_b}(Q_a, Q_b) = N_{v_a} N_{v_b} \exp[-\gamma({Q_a}^2 + {Q_b}^2)/2] H_{v_a}(\gamma^{1/2} Q_a) H_{v_b}(\gamma^{1/2} Q_b), \tag{11-139}$$

i.e.,

$$\Phi_{1,0} = (\gamma/2\pi)^{1/2} \exp[-\gamma({Q_a}^2 + {Q_b}^2)/2] 2\gamma^{1/2} Q_a \tag{11-140}$$

and

$$\Phi_{0,1} = (\gamma/2\pi)^{1/2} \exp[-\gamma({Q_a}^2 + {Q_b}^2)/2] 2\gamma^{1/2} Q_b \tag{11-141}$$

(both with energy $E = 2\hbar^2\gamma$) and

$$\Phi_{2,0} = (\gamma/8\pi)^{1/2} \exp[-\gamma({Q_a}^2 + {Q_b}^2)/2](4\gamma {Q_a}^2 - 2), \tag{11-142}$$

$$\Phi_{0,2} = (\gamma/8\pi)^{1/2} \exp[-\gamma({Q_a}^2 + {Q_b}^2)/2](4\gamma {Q_b}^2 - 2), \tag{11-143}$$

and

$$\Phi_{1,1} = (\gamma/4\pi)^{1/2} \exp[-\gamma({Q_a}^2 + {Q_b}^2)/2] 4\gamma Q_a Q_b \tag{11-144}$$

(all with energy $E = 3\hbar^2\gamma$), etc. Equations (11-137) and (11-139) give the energy levels and wavefunctions of the *two-dimensional (isotropic) harmonic oscillator Hamiltonian*

$$\hat{H}_{\mathrm{tdho}} = \frac{1}{2}[\hat{P}_a{}^2 + \hat{P}_b{}^2 + \lambda(Q_a{}^2 + Q_b{}^2)]. \tag{11-145}$$

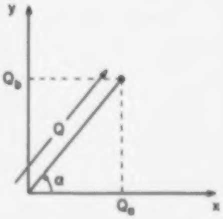

Fig. 11-2. A diagrammatic representation of the relationship between the coordinates (Q_a, Q_b) and (Q, α) given in Eqs. (11-146)-(11-149) for a two-dimensional isotropic harmonic oscillator.

For the two-dimensional harmonic oscillator we could use the wavefunctions as given in Eq. (11-139), but it proves more convenient to express them in terms of new coordinates Q and α, instead of Q_a and Q_b and to introduce new quantum numbers v and l instead of v_a and v_b. The coordinates Q and α are defined by

$$Q_a = Q\cos\alpha, \tag{11-146}$$

and

$$Q_b = Q\sin\alpha, \tag{11-147}$$

i.e.,

$$Q = \sqrt{Q_a{}^2 + Q_b{}^2}, \tag{11-148}$$

and

$$\alpha = \arctan(Q_b/Q_a) = \frac{1}{2}\arccos[(Q_a{}^2 - Q_b{}^2)/(Q_a{}^2 + Q_b{}^2)], \tag{11-149}$$

where $Q > 0$ and $0 \le \alpha \le 2\pi$. The relationship between these coordinates is represented in Fig. 11-2. Changing coordinates in Eq. (11-145) [using the chain rule, Eqs. (7-8) and (7-9)]

$$\hat{H}_{\mathrm{tdho}} = \frac{1}{2}\left[-\hbar^2\left(\frac{\partial^2}{\partial Q^2} + \frac{1}{Q}\frac{\partial}{\partial Q} + \frac{1}{Q^2}\frac{\partial^2}{\partial\alpha^2}\right) + \lambda Q^2\right] \tag{11-150}$$

[see also Boháček, Papoušek, Pick, and Špirko (1976)]. This operator commutes with the *vibrational angular momentum operator* $\hat{M}$ which is given by

$$\hat{M} = (Q_a\hat{P}_b - Q_b\hat{P}_a) = -i\hbar\frac{\partial}{\partial\alpha}, \tag{11-151}$$

and the eigenfunctions of $\hat{H}_{\text{tdho}}$ can be written

$$\Psi_{v,l} = F_{v,l}(Q)e^{il\alpha}, \tag{11-152}$$

where

$$\hat{M}\Psi_{v,l} = l\hbar\Psi_{v,l}, \tag{11-153}$$

and $F_{v,l}(Q)$ is a function only of Q. As we will see the vibrational angular momentum quantum number l can have any one of the $(v+1)$ values v, $v-2$, $v-4, \ldots, -v$.

The eigenfunctions and eigenvalues of $\hat{H}_{\text{tdho}}$ and the matrix elements of the normal coordinates and momenta can be determined using the ladder operator technique [see Moffitt and Liehr (1957)] and we will outline how the determination proceeds. We can rewrite $\hat{H}_{\text{tdho}}$ as

$$\hat{H}_{\text{tdho}} = \frac{1}{2}[\hat{P}^2 - i\hbar(1/Q)\hat{P} + (\hat{M}^2/Q^2) + \lambda Q^2] = \frac{1}{2}(\hat{P}^+\hat{P}^- + \lambda Q^+Q^-), \tag{11-154}$$

where

$$\hat{P} = -i\hbar\partial/\partial Q$$

and we have introduced

$$Q^{\pm} = Q_a \pm iQ_b = Qe^{\pm i\alpha} \tag{11-155}$$

and

$$\hat{P}^{\pm} = \hat{P}_a \pm i\hat{P}_b = e^{\pm i\alpha}[\hat{P} \pm i(\hat{M}/Q)]. \tag{11-156}$$

The appropriate ladder operators are

$$\hat{R}^{\pm(\pm)} = e^{(\pm)i\alpha}[P \pm i\lambda^{1/2}Q(\pm)i(M/Q)] = \hat{P}^{(\pm)} \pm i\lambda^{1/2}Q^{(\pm)}, \tag{11-157}$$

where the ± signs are correlated with each other and the (±) signs are also correlated with each other so that there are four ladder operators in all. The commutators of the ladder operators with $\hat{H}_{\text{tdho}}$ and $\hat{M}$ are

$$[\hat{H}_{\text{tdho}}, \hat{R}^{\pm(\pm)}] = \pm\hbar^2\gamma\hat{R}^{\pm(\pm)} \tag{11-158}$$

and

$$[\hat{M}, \hat{R}^{\pm(\pm)}] = (\pm)\hbar\hat{R}^{\pm(\pm)}. \tag{11-159}$$

The eigenvalues of $\hat{H}_{\text{tdho}}$ and $\hat{M}$ are E and $l\hbar$, respectively, so that

$\hat{R}^{+(+)}$	ladders E up by $\hbar^2\gamma$ and ladders l up by 1,
$\hat{R}^{+(-)}$	ladders E up by $\hbar^2\gamma$ and ladders l down by 1,
$\hat{R}^{-(+)}$	ladders E down by $\hbar^2\gamma$ and ladders l up by 1, and
$\hat{R}^{-(-)}$	ladders E down by $\hbar^2\gamma$ and ladders l down by 1.

In the notation of Moffitt and Liehr (1957) the four ladder operators are called $F, G^\dagger, G$, and $F^\dagger$ respectively. Equations like Eq. (11-102) can be set up for the lowest eigenfunction $\Psi_{0,l}$ of H_{tdho}, i.e.,

$$R^{+(+)}R^{-(-)}\Psi_{0,l} = (2H_{\mathrm{tdho}} + 2\lambda^{1/2}M - 2\hbar\lambda^{1/2})\Psi_{0,l} = 0 \tag{11-160}$$

and

$$R^{+(-)}R^{-(+)}\Psi_{0,l} = (2H_{\mathrm{tdho}} - 2\lambda^{1/2}M - 2\hbar\lambda^{1/2})\Psi_{0,l} = 0. \tag{11-161}$$

By adding and subtracting these two equations we determine that the lowest level is nondegenerate with

$$E_0 = \hbar^2\gamma \tag{11-162}$$

and

$$l = 0. \tag{11-163}$$

Solving

$$R^{-(-)}\Psi_{0,0} = 0 \tag{11-164}$$

gives

$$\Psi_{0,0} = (\gamma/\pi)^{1/2}\exp[-(\gamma Q^2/2)], \tag{11-165}$$

where the function is normalized and a real and positive phase factor choice has been adopted. We can write

$$\Psi_{v,l} = N'_{v,l}[\hat{R}^{+(-)}]^{(v-l)/2}[\hat{R}^{+(+)}]^{(v+l)/2}\Psi_{0,0}, \tag{11-166}$$

where $l = v, v-2, \ldots, -v$, and

$$E_v = (v+1)\hbar^2\gamma. \tag{11-167}$$

We can determine the matrix elements of $\hat{R}^{\pm(\pm)}$ in the functions $\Psi_{v,l}$, and from these the matrix elements of $Q^\pm$ and $\hat{P}^\pm$ (or $Q_a, Q_b, \hat{P}_a$, and $\hat{P}_b$) follow by using relations such as

$$\hat{P}^+ = [\hat{R}^{+(+)} + \hat{R}^{-(+)}]/2. \tag{11-168}$$

The nonvanishing matrix elements of $Q^\pm$ and $\hat{P}^\pm$ in the functions $\Psi_{v,l}$ are given in Table 11-3. We have changed the phase factor choice here from that used in Table 8-3 of Edition 1 [and in Moffitt and Liehr (1957)] so that the matrix elements of $Q^\pm$ are real and those of $P^\pm$ are imaginary. This accords with the choice made for the one-dimensional harmonic oscillator and is in agreement with the choice generally made in the literature. Blass (1969) gives a general discussion of the possible phase factor choices; the choice made here corresponds to his case B.

Table 11-3

Matrix elements of $Q^\pm$ and $\hat{P}^\pm$ for the two-dimensional isotropic harmonic oscillator[a]

$\langle v+1, l+1 \vert Q^+ \vert v, l \rangle = \sqrt{(v+l+2)/(2\gamma)}$	$\langle v+1, l+1 \vert \hat{P}^+ \vert v, l \rangle = i\hbar\sqrt{(v+l+2)\gamma/2}$
$\langle v+1, l-1 \vert Q^- \vert v, l \rangle = \sqrt{(v-l+2)/(2\gamma)}$	$\langle v+1, l-1 \vert \hat{P}^- \vert v, l \rangle = i\hbar\sqrt{(v-l+2)\gamma/2}$
$\langle v-1, l+1 \vert Q^+ \vert v, l \rangle = \sqrt{(v-l)/(2\gamma)}$	$\langle v-1, l+1 \vert \hat{P}^+ \vert v, l \rangle = -i\hbar\sqrt{(v-l)\gamma/2}$
$\langle v-1, l-1 \vert Q^- \vert v, l \rangle = \sqrt{(v+l)/(2\gamma)}$	$\langle v-1, l-1 \vert \hat{P}^- \vert v, l \rangle = -i\hbar\sqrt{(v+l)\gamma/2}$

[a] $Q^\pm = Q_a \pm iQ_b = Qe^{\pm i\alpha}$ and $\hat{P}^\pm = \hat{P}_a \pm i\hat{P}_b = e^{\pm i\alpha}(\hat{P} \pm i\hat{M}/Q)$ and the two-dimensional isotropic harmonic oscillator wavefunctions $\Psi_{v,l} = |v,l\rangle$. The phase factor choice is case B of Blass (1969); see text.

For a triply degenerate normal mode the harmonic oscillator eigenfunctions are written $\Psi_{v,l,n}(Q,\alpha,\beta)$, in a similar way to the preceding,[6] where l and n are vibrational angular momentum quantum numbers and α and β are vibrational angular coordinates. The harmonic oscillator energy is

$$E_v = \left(v + \frac{3}{2}\right)\hbar^2\gamma, \tag{11-169}$$

$v$where $v = 0, 1, 2, 3, \ldots$. The allowed values for l are

$$l = v, v-2, v-4, \ldots, 1 \text{ or } 0, \tag{11-170}$$

and the allowed values for n are

$$n = -l, -l+1, \ldots, l-1, l. \tag{11-171}$$

The complete vibrational wavefunctions of a molecule in the harmonic oscillator approximation is written as a product of one-, two-, and three-dimensional harmonic oscillator functions according to the symmetry degeneracies of the normal coordinates.

11.4 SUMMARY

As a result of making the Born-Oppenheimer approximation, and making the rigid rotor and harmonic oscillator approximations to the rotation-vibration Hamiltonian, we have obtained useful zero order Schrödinger equations for the rotation and vibration motions [see Eqs. (11-6) and (11-7)]. Using ladder operators [see Eqs. (11-30), (11-35), (11-89), (11-90), and (11-157)] we can determine the rotation and vibration basis wavefunctions, and important matrix elements. These matrix elements are tabulated in Tables 11-1 to 11-3. In the next chapter we show how these functions can be classified in the MS group, and in Chapter 13 we show how the effects of the breakdown of the various approximations made here are treated using these matrix elements.

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[6] See Eqs. (20)-(22) on page 355 in Wilson, Decius, and Cross (1955) or Section 5.4 in Papoušek and Aliev (1982). In these references, α, β are θ, ϕ.

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The vibrational Schrödinger equation

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12

The Symmetry of the Rovibronic Wavefunctions

We explain how the rovibronic coordinates and wavefunctions transform in the MS group, and we use the water and methyl fluoride molecules as examples. We introduce the concept of an equivalent rotation for an element of the MS group; this makes the determination of the transformation properties of the Euler angles, and the symmetry classification of the rotational wavefunctions, straightforward. We show how the symmetry species of the normal coordinates, and harmonic oscillator vibrational basis wavefunctions, in the MS group, can be determined. The transformation properties of molecular orbitals [including electron spin functions in Hund's cases (a) and (b)], and the symmetry of electronic wavefunctions, in the MS group are also discussed. At the end of the chapter, in a section on near symmetry, we explain the use of the molecular rotation group and the molecular point group.

12.1 THE TRANSFORMATION PROPERTIES OF THE ROVIBRATIONAL COORDINATES

For a rigid nonlinear molecule we need the transformation properties of the Euler angles, and the normal coordinates, under the effect of nuclear permutations and the inversion.

12.1.1 The transformation properties of the Euler angles

It is useful to determine the transformations that the Euler angles undergo when the (x, y, z) axes are rotated about various molecule-fixed axes. The rotation R_α^π of the (x, y, z) axes through π radians about an axis in the xy plane making an angle α with the x axis (α is measured in a right handed sense about the z axis) changes the Euler angles to $(\pi - \theta, \phi + \pi, 2\pi - 2\alpha - \chi)$. Similarly the rotation R_z^β by β radians about the z axis (measured in the right handed sense about z) changes the Euler angles to $(\theta, \phi, \chi + \beta)$. These results are given in Table 12-1 for easy reference. Knowing the transformation properties of the Euler angles, those of $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ are easily deduced [see Eqs. (10-84)-(10-86)] and are included in Table 12-1.

Each element of the MS group of a molecule causes a certain change in the Euler angles of the molecule, and these changes are straightforward to determine, as we will show below using the water and methyl fluoride molecules as examples. The change in the Euler angles can be represented as an *equivalent rotation*. For example, for the H_2O molecule discussed below the equivalent rotations of the operations E, (12), E^*, and $(12)^*$ are shown to be R^0, R_0^π, $R_{\pi/2}^\pi$, and R_z^π, respectively, where we use the notation of Table 12-1, and R^0 is the identity. We can alternatively write these equivalent rotations as R^0, R_x^π, R_y^π and R_z^π, or as R^0, R_b^π, R_c^π and R_a^π, respectively.[1]

In the character tables in Appendix ***A*** equivalent rotations of the elements are given. For symmetric top molecules we use the notation R_α^π and R_z^β (as in Table 12-1) for the equivalent rotations, but for asymmetric top molecules we use the notation R_a^π, R_b^π and R_c^π.

Below we determine the effects of the MS group elements on the Euler angles for the water and methyl fluoride molecules as examples and we use simple figures to do this. The results can be obtained using the equations that define the Euler angles, and this is done in Appendix 12-1.

Table 12-1

The transformation properties[a] of the Euler angles and of the components of the rovibronic angular momentum $\hat{\boldsymbol{J}}$

	R_α^π	R_z^β
θ	$\pi - \theta$	θ
ϕ	$\phi + \pi$	ϕ
χ	$2\pi - 2\alpha - \chi$	$\chi + \beta$
$\hat{J}_x$	$\hat{J}_x \cos 2\alpha + \hat{J}_y \sin 2\alpha$	$\hat{J}_x \cos\beta + \hat{J}_y \sin\beta$
$\hat{J}_y$	$\hat{J}_x \sin 2\alpha - \hat{J}_y \cos 2\alpha$	$-\hat{J}_x \sin\beta + \hat{J}_y \cos\beta$
$\hat{J}_z$	$-\hat{J}_z$	$\hat{J}_z$

[a] R_α^π is a rotation of the molecule fixed (x, y, z) axes through π radians about an axis in the xy plane making an angle α with the x axis (α is measured in the right handed sense about the z axis), and R_z^β is a rotation of the molecule fixed (x, y, z) axes through β radians about the z axis (β is measured in the right handed sense about the z axis). The expressions for the $\hat{J}_\alpha$ are given in Eqs. (10-84)-(10-86).

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[1] See the discussion given in connection with Fig. 10-2 on page 210 for the definition of the relation between the xyz and abc axes for the water molecule.

EXAMPLE USING THE WATER MOLECULE

The effect of the permutation (12) on a water molecule in its equilibrium configuration is shown in Fig. 12-1. In this figure we *first* permute the nuclei and *then* use the prescription discussed before Eq. (10-38) to attach the (x, y, z) axes. The permutation of identical nuclei in a molecule does not change the orientation of the principal axes in space since identical nuclei have the same mass. However, the choice of which of the molecule fixed axes is to be identified with which principal axis and the choice of sign for the x, y, and z axes depends on the labels on the nuclei. We see that in the water molecule the molecule fixed (x, y, z) axes are rotated by π radians about the x axis by (12), and the change in the Euler angles caused by this is

$$(12)(\theta, \phi, \chi) = R_0{}^{\pi}(\theta, \phi, \chi) = (\pi - \theta, \phi + \pi, 2\pi - \chi). \qquad (12\text{-}1)$$

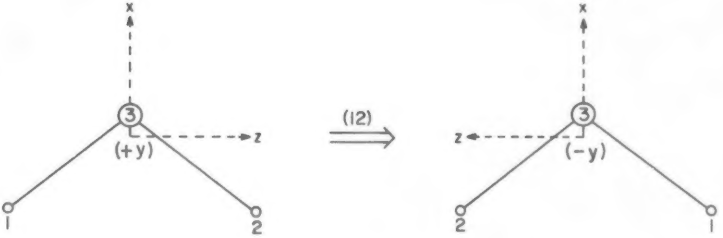

Fig. 12-1. The effect of the nuclear permutation (12) on the nuclei of a water molecule in its equilibrium configuration. The molecule fixed axes are attached afterwards using the convention of Fig. 10-2.

The effect of E^* on a water molecule is shown in Fig. 12-2 and the (x, y, z) axes have been attached after performing E^* by using the prescription for attaching the axes given before Eq. (10-38). This operation for a water molecule has the effect of rotating the axes by π radians about the y axis, and using $R_{\pi/2}{}^{\pi}$ from Table 12-1 we deduce that

$$E^*(\theta, \phi, \chi) = R_{\pi/2}{}^{\pi}(\theta, \phi, \chi) = (\pi - \theta, \phi + \pi, \pi - \chi). \qquad (12\text{-}2)$$

The successive application of E^* and (12) for a water molecule leads to a rotation of the molecule by π radians about the z axis. Using $R_z{}^{\pi}$ from Table 12-1 we have

$$(12)^*(\theta, \phi, \chi) = R_z{}^{\pi}(\theta, \phi, \chi) = (\theta, \phi, \chi + \pi). \qquad (12\text{-}3)$$

Our choice for the way of locating the xyz axes on the water molecule has $xyz{=}bca$ (see the discussion given in connection with Fig. 10-2 on page 210).

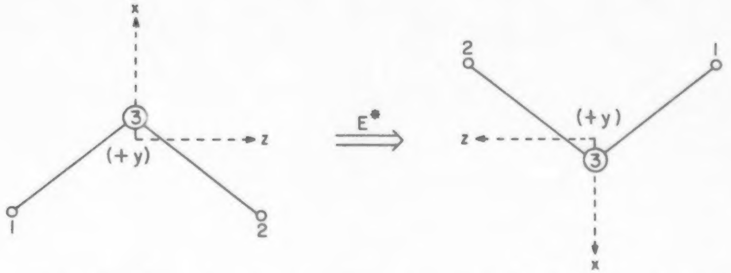

Fig. 12-2. The effect of the inversion E^* on the nuclei of a water molecule in its equilibrium configuration. The molecule fixed axes are attached afterwards using the convention of Fig. 10-2.

Thus the equivalent rotations of the operations of the MS group of the water molecule $\{E, (12), E^*, (12)^*\}$ are R^0, R_b^π, R_c^π and R_a^π, respectively.

EXAMPLE USING THE METHYL FLUORIDE MOLECULE

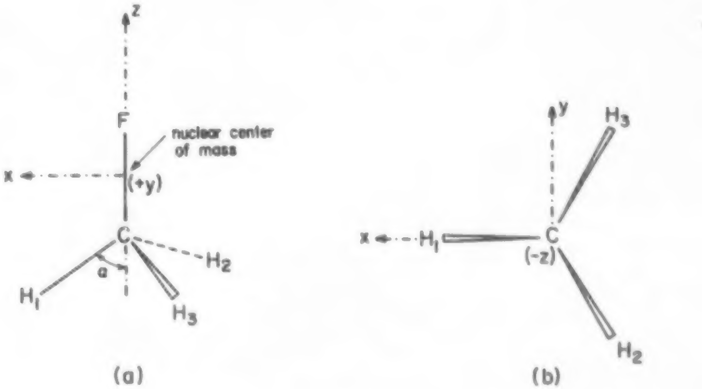

Fig. 12-3. The nuclear labeling convention and (x, y, z) axis definition for a CH_3F molecule in its equilibrium configuration. In (b) the three protons are above the plane of the page and the z axis points down into the page.

We determine the equivalent rotations of the MS group elements (123) and $(23)^*$. In Fig. 12-3 we show two views of a methyl fluoride molecule in its equilibrium configuration with the molecule fixed (x, y, z) axes attached. In Fig. 12-4 we show the effect of the operations (123) and $(23)^*$ on the molecule, using view (b) of Fig. 12-3 as the starting position. After having performed the MS group operations the (x, y, z) axes are attached following the convention of Fig. 12-3. It is obvious that (123) has resulted in the molecule fixed axes being rotated in a right handed sense through $2\pi/3$ radians about the z axis, and that $(23)^*$ has resulted in the axes being rotated through π radians about the y axis. The equivalent rotations of (123) and $(23)^*$ are $R_z^{2\pi/3}$ and $R_{\pi/2}^{\pi}$, respectively, and we can write

$$(123)(\theta,\phi,\chi) = R_z^{2\pi/3}(\theta,\phi,\chi) = (\theta,\phi,\chi + 2\pi/3) \qquad (12\text{-}4)$$

and

$$(23)^*(\theta,\phi,\chi) = R_{\pi/2}^{\pi}(\theta,\phi,\chi) = (\pi - \theta, \phi + \pi, \pi - \chi). \qquad (12\text{-}5)$$

The transformation properties of the Euler angles are obtained from Fig. 12-4.

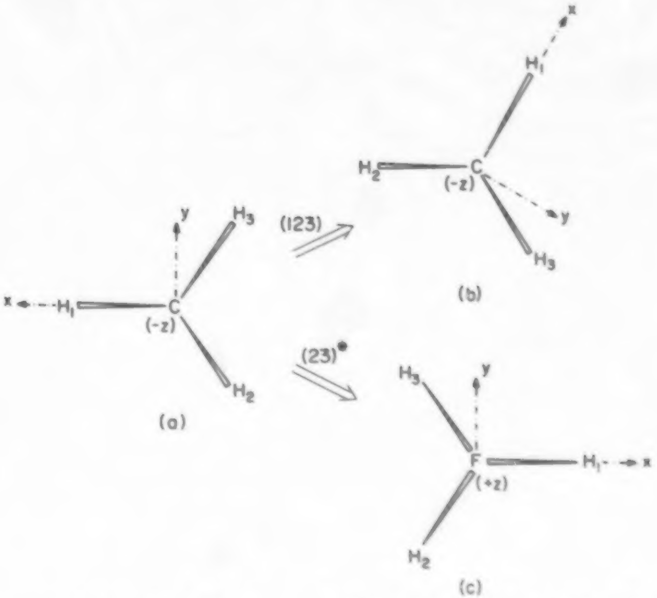

Fig. 12-4. The effects of the operations (123) and $(23)^*$ on a CH_3F molecule in its equilibrium configuration. In (c) the three protons are below the plane of the page and the z axis points up out of the page.

12.1.2 The transformation properties of the normal coordinates

In Chapter 10 we introduced the the three translational coordinates T_x, T_y, and T_z defined by Eq. (10-111), and the three rotational coordinates R_x, R_y, and R_z defined by Eq. (10-112). These are the six zero frequency normal coordinates and

$$[R_x, R_y, R_z, T_x, T_y, T_z] = [Q_{3N-5}, Q_{3N-4}, \ldots, Q_{3N}]. \qquad (12\text{-}6)$$

We can rewrite Eq. (10-134) as

$$\Delta\alpha_i = \sum_{r=1}^{3N} m_i^{-1/2} l_{\alpha i,r} Q_r. \qquad (12\text{-}7)$$

which means that the transformation from the $3N$ $\Delta\alpha_i$ to the $3N$ Q_r is orthogonal. Thus the $3N$ Q_r will generate the same representation of the symmetry group as do the $3N$ $\Delta\alpha_i$ [see Eq. (6-54) and remarks after it]. To determine the representation generated by the $3N - 6$ normal coordinates Q_r we must determine the representation generated by the $3N$ Cartesian displacement coordinates $\Delta\alpha_i$ and then subtract the representation generated by the three R_α and three T_α. An alternative procedure for determining the species of the normal coordinates involves using internal coordinate displacements (bond stretches, angle bends, etc.) rather than Cartesian displacement coordinates, and this will be explained using the water and methane molecules as examples.

The determination of the representation of the group generated by the zero frequency normal coordinates R_α and T_α does not require that we determine the coordinates as done below in Eq. (12-15) for the water molecule. In Appendix 12-2 we show that the R_α transform in the same way as the J_α, and that the representation generated by the T_α is obtained from that generated by the J_α by changing the signs of the characters for all permutation-inversion operations. The representation generated by the J_α can be determined from the results in Table 12-1 once the equivalent rotations of the elements of the group have been determined. For spherical top molecules the operators (J_x, J_y, J_z) transform as the representation $D^{(1)}$ of the group $\boldsymbol{K}$(mol). From the correlation of the species of $\boldsymbol{K}$(mol) with the species of the MS group the species of (J_x, J_y, J_z) in the MS group for any spherical top molecule can be determined. It should be noted that for any molecule the species of the components of the vibrational angular momentum (p_x, p_y, p_z), the components of the electronic orbital angular momentum (L_x, L_y, L_z), and the components in one column of the direction cosine matrix $(\lambda_{x\tau}, \lambda_{y\tau}, \lambda_{z\tau})$, where $\tau = \xi$, η or ζ, are the same as those of (J_x, J_y, J_z).

The species of the J_α, which equals that of the R_α, and of the T_α are given for each MS group in the character tables of Appendix $\boldsymbol{A}$.

The transformation properties of these various terms in the molecular point group can also be determined. For nonlinear rigid molecules (R_x, R_y, R_z), (T_x, T_y, T_z), (L_x, L_y, L_z) and (p_x, p_y, p_z) transform in the same way in the point group as they do in the isomorphic MS group. However, since the elements of the molecular point group do not transform the Euler angles the (J_x, J_y, J_z) and the direction cosine matrix elements are not transformed by the elements of the point group.

EXAMPLE USING THE WATER MOLECULE

To determine the symmetry species of the normal coordinates of water in the $\boldsymbol{C}_{2v}$(M) group (see Table 6-2) we begin by determining the transformation

F4

properties of the Cartesian displacement coordinates under the effect of the symmetry operations of $\boldsymbol{C}_{2v}(\mathrm{M})$. From these transformation properties we can determine the representation of the $\boldsymbol{C}_{2v}(\mathrm{M})$ group generated by the Cartesian displacement coordinates; we will call this representation Γ_{Car}. Once again we have the option of obtaining the results by studying figures or by studying equations. We do not need to do either to see that the character under the identity E in Γ_{Car} using the nine $(\Delta x_1, \ldots, \Delta z_3)$ is

$$\chi[E] = 9. \tag{12-8}$$

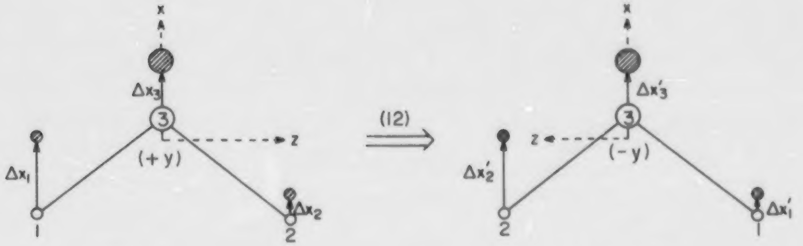

Fig. 12-5. The effect of the nuclear permutation (12) on the Cartesian displacements Δx_i in a water molecule. The new values $(\Delta x_i{}')$ are related to the old values (Δx_i) by $\Delta x_1{}' = \Delta x_2, \Delta x_2{}' = \Delta x_1$, and $\Delta x_3{}' = \Delta x_3$.

The effect of the operation (12) is depicted in Fig. 12-5 where Cartesian displacements of the nuclei have been added. We see that

$$(12)(\Delta x_1, \Delta x_2, \Delta x_3) = (\Delta x_1{}', \Delta x_2{}', \Delta x_3{}') = (\Delta x_2, \Delta x_1, \Delta x_3). \tag{12-9}$$

Since the y and z axes are reversed by (12) and the nuclei 1 and 2 permuted we have

$$\begin{aligned}(12)&(\Delta y_1, \Delta z_1, \Delta y_2, \Delta z_2, \Delta y_3, \Delta z_3)\\ &= (\Delta y_1{}', \Delta z_1{}', \Delta y_2{}', \Delta z_2{}', \Delta y_3{}', \Delta z_3{}')\\ &= (-\Delta y_2, -\Delta z_2, -\Delta y_1, -\Delta z_1, -\Delta y_3, -\Delta z_3).\end{aligned} \tag{12-10}$$

As a result we obtain the character in Γ_{Car} under (12) as

$$\chi[(12)] = -1. \tag{12-11}$$

To use equations instead of figures we start by writing

$$\Delta\alpha_i = \alpha_i - \alpha_i{}^e = (\lambda_{\alpha\xi}\xi_i + \lambda_{\alpha\eta}\eta_i + \lambda_{\alpha\zeta}\zeta_i) - \alpha_i{}^e. \tag{12-12}$$

The direction cosines are functions of the Euler angles [see Eq. (10-7)] and we can determine the effect of (12) on them from the results in Eqs. (12-1) or (12-112). The effect of (12) on the (ξ_i, η_i, ζ_i) is obtained from Eq. (12-110). The α_i^e are constants [see Eq. (10-38)] and are unaffected by any symmetry operation. We see that

$$\begin{aligned}(12)\Delta z_1 = \Delta z_1' &= \sin\theta'\cos\phi'\xi_1' + \sin\theta'\sin\phi'\eta_1' + \cos\theta'\zeta_1' - z_1^e \\ &= -\sin\theta\cos\phi\xi_2 - \sin\theta\sin\phi\eta_2 - \cos\theta\zeta_2 + 0.7592\ \text{Å} \\ &= -z_2 + 0.7592\ \text{Å} = -\Delta z_2, \qquad (12\text{-}13)\end{aligned}$$

where we have used the result that $-z_1^e = z_2^e = 0.7592$ Å.

The transformation properties of the Cartesian displacement coordinates under the effect of E^* and $(12)^*$ can be similarly determined and the results are collected together in Table 12-2. The characters of the representation Γ_{Car} are also given in Table 12-2 and using Eq. (5-45) we express this in terms of irreducible representations as:

$$\Gamma_{\text{Car}} = 3A_1 \oplus A_2 \oplus 2B_1 \oplus 3B_2. \qquad (12\text{-}14)$$

Table 12-2

The transformation properties of the coordinates in the $C_{2v}(\text{M})$ group for the water molecule

	E	(12)	E^*	$(12)^*$	E	(12)	E^*	$(12)^*$	
	Δx_1	Δx_2	Δx_1	Δx_2	T_x	T_x	T_x	T_x	$: A_1$
	Δx_2	Δx_1	Δx_2	Δx_1	T_y	$-T_y$	$-T_y$	T_y	$: B_1$
	Δx_3	Δx_3	Δx_3	Δx_3	T_z	$-T_z$	T_z	$-T_z$	$: B_2$
	Δy_1	$-\Delta y_2$	$-\Delta y_1$	Δy_2	R_x	R_x	$-R_x$	$-R_x$	$: A_2$
	Δy_2	$-\Delta y_1$	$-\Delta y_2$	Δy_1	R_y	$-R_y$	R_y	$-R_y$	$: B_2$
	Δy_3	$-\Delta y_3$	$-\Delta y_3$	Δy_3	R_z	$-R_z$	$-R_z$	R_z	$: B_1$
	Δz_1	$-\Delta z_2$	Δz_1	$-\Delta z_2$					
	Δz_2	$-\Delta z_1$	Δz_2	$-\Delta z_1$					
	Δz_3	$-\Delta z_3$	Δz_3	$-\Delta z_3$					
χ_{Car}:	9	-1	3	1					

To determine the character in Γ_{Car} under the effect of a permutation or permutation-inversion we only need consider the transformations of the coordinates of unpermuted nuclei since these will give the only nonvanishing contributions on the diagonal of the representation matrix. Thus to determine the character in Γ_{Car} under the effect of (12) or $(12)^*$ we only need consider the transformations of the coordinates Δx_3, Δy_3, and Δz_3 in the water molecule.

Using Eqs. (10-111) and (10-112) we obtain (in $u^{1/2}$ Å units)

$$\begin{aligned}
T_x &= (\Delta x_1 + \Delta x_2 + 16\Delta x_3)/18^{1/2}, \\
T_y &= (\Delta y_1 + \Delta y_2 + 16\Delta y_3)/18^{1/2}, \\
T_z &= (\Delta z_1 + \Delta z_2 + 16\Delta z_3)/18^{1/2}, \\
R_x &= (\Delta y_1 - \Delta y_2)/2^{1/2}, \qquad (12\text{-}15) \\
R_y &= 0.3907[1.466(\Delta x_2 - \Delta x_1) + \Delta z_1 + \Delta z_2 - 2\Delta z_3],
\end{aligned}$$

and

$$R_z = 2(-\Delta y_1 - \Delta y_2 + 2\Delta y_3)/3.$$

The transformation properties of these coordinates can be determined from the transformation properties of the $\Delta\alpha_i$ coordinates given in Table 12-2 and the results are given in the bottom half of Table 12-2. We see that for H_2O

$$\Gamma(R_x, R_y, R_z) = A_2 \oplus B_2 \oplus B_1 \tag{12-16}$$

$$\Gamma(T_x, T_y, T_z) = A_1 \oplus B_1 \oplus B_2. \tag{12-17}$$

This conforms to the general rule that the symmetry species of R_α is the same as that of J_α (see Table A-5), and that the transformation properties of T_α is the same as that of R_α but with the signs for the permutation-inversion operations reversed. Subtracting the sum of Eq. (12-16) and Eq. (12-17) from Eq. (12-14) we determine that the normal coordinate representation is

$$\Gamma(Q_1, Q_2, Q_3) = 2A_1 \oplus B_2. \tag{12-18}$$

As we explained below Eq. (11-136) the normal coordinates each transform according to an irreducible representation of the symmetry group and we have

$$\Gamma(Q_1) = \Gamma(Q_2) = A_1 \tag{12-19}$$

and

$$\Gamma(Q_3) = B_2. \tag{12-20}$$

Problem 12-1. We have determined in Section 10.2.1 [see Eq. (10-56)] and in Section 10.4.4 [see Eq. (10-147)] that a deformed water molecule having nuclear coordinates given as in Eq. (10-52) has rovibrational coordinates given by (where Q_r is in $u^{1/2}$ Å)

$$(\theta, \phi, \chi, Q_1, Q_2, Q_3) = (30°, 60°, 120°, 1, 0, 1). \tag{12-21}$$

If we permute the two protons the (ξ, η, ζ) coordinates of nuclei H_1, H_2, and O_3 become

$$(0.6760, 0.3138, 0.5614), \qquad (0.8136, -0.8891, -1.9562), \\ \text{and} \qquad (-0.0930, 0.0360, 0.0872), \tag{12-22}$$

respectively. Use the methods of Eqs (10-52)-(10-147) to determine the values of the rovibrational coordinates for the deformed water molecule represented in Eq. (12-22). Check the answer against the results obtained from Eqs. (12-1), (12-19), and (12-20) for the effect of (12).

Answer. We first use the Eckart equations, Eqs. (10-34)-(10-36), to determine the Euler angles. The $[\alpha\tau]$ factors are evaluated from the equilibrium nuclear coordinates of Eq. (10-38) and the (ξ, η, ζ) coordinates of Eq. (12-22). Doing this we obtain Eqs. (10-53) and (10-54) as before, but Eq. (10-36) does not give Eq. (10-55) and instead we obtain

$$\begin{aligned} &+ 0.1045(\cos\theta\cos\phi\cos\chi - \sin\phi\sin\chi) - 0.9132(\cos\theta\sin\phi\cos\chi + \cos\phi\sin\chi) \\ &\quad + 1.9114\sin\theta\cos\chi + 0.8676\sin\theta\cos\phi - 0.3352\sin\theta\sin\phi \\ &\quad - 0.8125\cos\theta = 0. \end{aligned} \tag{12-23}$$

Solving Eqs. (10-53), (10-54), and (12-23) simultaneously we obtain

$$(\theta, \phi, \chi) = (150^\circ, 240^\circ, 240^\circ), \tag{12-24}$$

which differs from the Euler angles of Eq. (12-21) according to the result of Eq. (12-1); hence the molecule fixed axes of the distorted molecule are rotated through π radians about the x axis by (12).

From these Euler angles we can determine the (x, y, z) nuclear coordinates from the (ξ, η, ζ) coordinates in Eq. (12-22) by using the direction cosines, i.e., Eq. (10-5). The (x, y, z) coordinates of nuclei 1, 2, and 3, respectively, are found to be (compare with Eq. (10-68))

$$(-0.4948, 0, -0.7911), \quad (-1.3270, 0, 1.8757), \quad (0.1138, 0, -0.0678). \tag{12-25}$$

From Eqs. (12-25) and (10-38) we determine the Cartesian displacement coordinates, and using the inverse of Eq. (10-146) we determine the values of the normal coordinates to be (where Q_r is in $u^{1/2}$ Å)

$$(Q_1, Q_2, Q_3) = (1, 0, -1), \tag{12-26}$$

which agrees with Eqs. (12-19) and (12-20).

Since the $(3N-6)$ normal coordinates Q_r are linearly independent, as are the $(3N-6)$ internal coordinate displacements $\mathcal{R}_i$ [see Eq. (10-102)], and since each nonvanishing term in the sum in Eq. (10-139) (which expresses the $\mathcal{R}_i$ in terms of the Q_r) must have the same symmetry species in a symmetry group of the vibrational Hamiltonian, we see that the symmetry species of the Q_r is the same as that of the $\mathcal{R}_i$. As a result it is possible to determine the symmetry of the normal coordinates in a molecule by determining the symmetry of the $(3N-6)$ independent internal coordinate displacements (bond stretches, angle bends, etc.). This is often simpler than determining the symmetry of the Q_r from the symmetry of the Cartesian displacement coordinates. However, one must use $(3N-6)$ independent $\mathcal{R}_i$ coordinates and avoid combinations of internal coordinates that are redundant.

For the water molecule the $\mathcal{R}_i$ are defined in Eq. (10-103) and it is simple to determine that

$$\Gamma(\mathcal{R}_1, \mathcal{R}_2, \mathcal{R}_3) = 2A_1 \oplus B_2. \tag{12-27}$$

This is the species of the normal coordinates.

Table 12-3

Transformation properties of the internal coordinates of methane in $\boldsymbol{T}_d(\mathrm{M})$

E	(123)	(14)(23)	(1423)	(23)*
Δr_1	Δr_3	Δr_4	Δr_3	Δr_1
Δr_2	Δr_1	Δr_3	Δr_4	Δr_3
Δr_3	Δr_2	Δr_2	Δr_2	Δr_2
Δr_4	Δr_4	Δr_1	Δr_1	Δr_4
$\Delta\alpha_{12}$	$\Delta\alpha_{13}$	$\Delta\alpha_{34}$	$\Delta\alpha_{34}$	$\Delta\alpha_{13}$
$\Delta\alpha_{13}$	$\Delta\alpha_{23}$	$\Delta\alpha_{24}$	$\Delta\alpha_{23}$	$\Delta\alpha_{12}$
$\Delta\alpha_{14}$	$\Delta\alpha_{34}$	$\Delta\alpha_{14}$	$\Delta\alpha_{13}$	$\Delta\alpha_{14}$
$\Delta\alpha_{23}$	$\Delta\alpha_{12}$	$\Delta\alpha_{23}$	$\Delta\alpha_{24}$	$\Delta\alpha_{23}$
$\Delta\alpha_{24}$	$\Delta\alpha_{14}$	$\Delta\alpha_{13}$	$\Delta\alpha_{14}$	$\Delta\alpha_{34}$
$\Delta\alpha_{34}$	$\Delta\alpha_{24}$	$\Delta\alpha_{12}$	$\Delta\alpha_{12}$	$\Delta\alpha_{24}$

As another example we will determine the symmetry species of the normal coordinates of methane. We use the following internal coordinate displacement coordinates $\mathcal{R}_i$:

$$\Delta r_1, \Delta r_2, \Delta r_3, \Delta r_4, \quad \Delta\alpha_{12}, \Delta\alpha_{13}, \Delta\alpha_{14}, \Delta\alpha_{23}, \Delta\alpha_{24}, \Delta\alpha_{34}, \tag{12-28}$$

where to first order the redundant combination of these coordinates is

$$R_{\mathrm{red}} = \sum_{i<j} \Delta\alpha_{ij} = 0, \tag{12-29}$$

where $\Delta\alpha_{ij}$ is an increase in the bond angle $\mathrm{H}_i\mathrm{CH}_j$ and Δr_i is an increase in the bond length CH_i. The transformation properties of these coordinates are given in Table 12-3. By subtracting the species of R_{red} (i.e., A_1) from that of the ten displacement coordinates in Eq. (12-28) we see that the normal coordinate representation is

$$\Gamma(Q_r) = A_1 \oplus E \oplus 2F_2 \tag{12-30}$$

and we can write the species of the normal coordinates as

$$\Gamma^{(1)} = A_1, \quad \Gamma^{(2)} = E, \quad \Gamma^{(3)} = F_2, \quad \text{and} \quad \Gamma^{(4)} = F_2. \tag{12-31}$$

For a symmetric top or spherical top molecule some of the normal coordinates will transform according to a degenerate representation of the MS group. In these circumstances a convention has to be adopted for the relative sense of the degenerate coordinates, and for symmetric top molecules the convention adopted is that due to di Lauro and Mills (1966). In determining off-diagonal matrix elements it is important that these relative transformation properties be well defined. We will explain how it is that we have such a freedom of choice.

If we consider a pair of normal coordinate (Q_{ta}, Q_{tb}) that transform according to a doubly degenerate irreducible representation, the effect of the MS group operations R on these coordinates is given by [see also Eqs. (11-131) and (11-132)]

$$\begin{aligned} R\begin{bmatrix} Q_{ta} \\ Q_{tb} \end{bmatrix} &= \begin{bmatrix} U_{11}^{(t)}(R)Q_{ta} + U_{12}^{(t)}(R)Q_{tb} \\ U_{21}^{(t)}(R)Q_{ta} + U_{22}^{(t)}(R)Q_{tb} \end{bmatrix} \\ &= \begin{bmatrix} U_{11}^{(t)}(R) & U_{12}^{(t)}(R) \\ U_{21}^{(t)}(R) & U_{22}^{(t)}(R) \end{bmatrix} \begin{bmatrix} Q_{ta} \\ Q_{tb} \end{bmatrix} = \mathbf{U}^{(t)}(R) \begin{bmatrix} Q_{ta} \\ Q_{tb} \end{bmatrix}. \end{aligned} \tag{12-32}$$

The 2×2 matrices $\mathbf{U}^{(t)}(R)$ [where R runs over the operations in the MS group] form a representation of the MS group as explained in Chapter 5. We can consider another set of normal coordinates (Q'_{ta}, Q'_{tb}) obtained from the original normal coordinates as follows:

$$\begin{bmatrix} Q'_{ta} \\ Q'_{tb} \end{bmatrix} = \mathbf{V} \begin{bmatrix} Q_{ta} \\ Q_{tb} \end{bmatrix}, \tag{12-33}$$

where $\mathbf{V}$ is an orthogonal, 2×2 matrix [see Table 5-1]. The effect of R on (Q'_{ta}, Q'_{tb}) is given by

$$R\begin{bmatrix} Q'_{ta} \\ Q'_{tb} \end{bmatrix} = \mathbf{V}\mathbf{U}^{(t)}(R)\mathbf{V}^{-1} \begin{bmatrix} Q'_{ta} \\ Q'_{tb} \end{bmatrix} = \grave{\mathbf{U}}^{(t)}(R) \begin{bmatrix} Q'_{ta} \\ Q'_{tb} \end{bmatrix}. \tag{12-34}$$

The new set of two × two matrices $\grave{\mathbf{U}}^{(t)}(R)$ also form a representation of the MS group, and this representation is equivalent to that formed by the matrices $\mathbf{U}^{(t)}(R)$ in the sense explained in Chapter 5. Using the orthogonality of $\mathbf{V}$ [Table 5-1]

$$(Q'_{ta})^2 + (Q'_{tb})^2 = Q_{ta}^2 + Q_{tb}^2. \tag{12-35}$$

An analogous equation is valid for the momenta (P'_{ta}, P'_{tb}) and (P_{ta}, P_{tb}).

Hence it does not matter if we use the normal coordinates (Q_{ta}, Q_{tb}) with conjugate momenta (P_{ta}, P_{tb}), or the normal coordinates (Q'_{ta}, Q'_{tb}) with conjugate momenta (P'_{ta}, P'_{tb}), to describe the normal mode ν_t of the molecule. We can simply replace (Q_{ta}, Q_{tb}) by (Q'_{ta}, Q'_{tb}), and (P_{ta}, P_{tb}) by (P'_{ta}, P'_{tb}), in the zero order vibrational Hamiltonian [Eq. (11-1a), see also Eq. (11-145)], and we can convert the complete rotation-vibration Hamiltonian to depend on these new quantities, without causing any real change in our theoretical description of the molecular vibration and rotation. That is, we have some freedom in defining the normal coordinates used to describe the degenerate normal modes.

It follows from Eq. (12-34) that for a degenerate normal mode, the transformation properties of the normal coordinates under the operations of the MS group are not unambiguously determined by the characters of the irreducible representation. In Eq. (12-34) we are free to choose the orthogonal matrix $\mathbf{V}$, and by changing this matrix we can change the transformation matrices $\tilde{\mathbf{U}}^{(t)}(R)$. The convention adopted for $\mathbf{V}$ [di Lauro and Mills (1966)] is defined by Eqs. (12-69)-(12-72) below which we express after we have introduced the concept of generating operations. Using this convention a pair of degenerate normal coordinates (Q_{ta}, Q_{tb}) of a C_{3v} molecule such as CH_3F transforms in the same way as (T_x, T_y) in the symmetry group. Using this convention we give the transformation properties of the normal coordinates of a C_{3v} molecule in Table 12-4 (where z is the three-fold axis and xz is one of the three reflection planes); in this table we include the transformation properties of the angular momentum components. In general, for a symmetric top molecule, it is an advantage to express the Hamiltonian in terms of $Q_t^{\pm} = Q_{ta} \pm Q_{tb}$ and $\hat{J}_m^{\pm}$, rather than Q_{ta}, Q_{tb}, $\hat{J}_x$ and $\hat{J}_y$, since they have simpler transformation properties.

12.2 THE CLASSIFICATION OF THE ROTATIONAL WAVEFUNCTIONS

The expression for the symmetric top wavefunction $|J, k, m\rangle$ in terms of the angular momentum ladder operators and the function $|J, 0, 0\rangle$ is given in Eqs (11-39) and (11-40). For an asymmetric top molecule the rotational eigenfunctions are linear combinations of symmetric top functions (see Problem 11-2 on page 248). We will determine the general effect of the rotation operations R_z^{β} and R_{α}^{π} on any symmetric top function $|J, k, m\rangle$ by determining their effect on the ladder operators and on the function $|J, 0, 0\rangle$. This will allow us to determine the transformation properties of any symmetric top or asymmetric top wavefunction in an MS group once we have identified the equivalent rotation of the MS group operation. The symmetries of spherical top wavefunctions are obtained by reduction of the representations of the group $\boldsymbol{K}$(mol). In this section we only consider states having J integral. The classification of rotational wavefunctions having J half-integral will be discussed in Section 18.5.

Table 12-4

The transformation properties of the normal coordinates and angular momentum components for a C_{3v} molecule[a]

	E	(123)	$(23)^*$	
Equiv. rot.	R^0	$R_z^{2\pi/3}$	$R^{\pi}_{\pi/2}$	
	Q_p	Q_p	Q_p	$: A_1$
	Q_{ta}	$cQ_{ta} + sQ_{tb}$	Q_{ta}	$: E$
	Q_{tb}	$cQ_{tb} - sQ_{ta}$	$-Q_{tb}$	
	Q_t	Q_t	Q_t	
	$\exp(i\alpha_t)$	$\omega^2 \exp(i\alpha_t)$	$\exp(-i\alpha_t)$	
	$Q_t{}^+$	$\omega^2 Q_t{}^+$	$Q_t{}^-$	$: E$
	$Q_t{}^-$	$\omega Q_t{}^-$	$Q_t{}^+$	
	$\hat{J}_x$	$c\hat{J}_x + s\hat{J}_y$	$-\hat{J}_x$	$: E$
	$\hat{J}_y$	$c\hat{J}_y - s\hat{J}_x$	$\hat{J}_y$	
	$\hat{J}_z$	$\hat{J}_z$	$-\hat{J}_z$	$: A_2$
	$\hat{J}_m{}^+$	$\omega^2 \hat{J}_m{}^+$	$-\hat{J}_m{}^-$	$: E$
	$\hat{J}_m{}^-$	$\omega \hat{J}_m{}^-$	$-\hat{J}_m{}^+$	

[a] $p = 1, 2$ or 3; $t = 4, 5$ or 6; $c = \cos(2\pi/3)$; $s = \sin(2\pi/3)$; $\omega = \exp(2\pi i/3) = c + i\,s$; $\omega^2 = \exp(-2\pi i/3) = c - i\,s$. $Q_{ta} = Q_t \cos\alpha_t$ and $Q_{tb} = Q_t \sin\alpha_t$. $Q_t{}^{\pm} = Q_{ta} \pm iQ_{tb}$ and $\hat{J}_m{}^{\pm} = \hat{J}_x \pm i\hat{J}_y$.

Using the rotational ladder operators $\hat{J}_m^{\pm}$ defined in Eq. (11-30), we obtain the following operator equations (each of which is two equations)

$$\begin{aligned} R_z{}^{\beta} \hat{J}_m{}^{\pm} &= [(\hat{J}_x \cos\beta + \hat{J}_y \sin\beta) \pm i(\hat{J}_y \cos\beta - \hat{J}_x \sin\beta)] R_z{}^{\beta} \\ &= [\cos\beta \hat{J}_m{}^{\pm} \mp i \sin\beta \hat{J}_m{}^{\pm}] R_z{}^{\beta} \\ &= e^{\mp i\beta} \hat{J}_m{}^{\pm} R_z{}^{\beta} \end{aligned} \tag{12-36}$$

and

$$\begin{aligned} R_{\alpha}{}^{\pi} \hat{J}_m{}^{\pm} &= [(\hat{J}_x \cos 2\alpha + \hat{J}_y \sin 2\alpha) \pm i(\hat{J}_x \sin 2\alpha - \hat{J}_y \cos 2\alpha)] R_{\alpha}{}^{\pi} \\ &= e^{\pm i2\alpha} \hat{J}_m{}^{\mp} R_{\alpha}{}^{\pi}. \end{aligned} \tag{12-37}$$

Clearly the space fixed axes are unaffected by $R_z{}^{\beta}$ and $R_{\alpha}{}^{\pi}$ so that for the ladder operators $\hat{J}_s{}^{\pm}$ [defined in Eq. (11-35)] we have the operator equations

$$R_z{}^{\beta} \hat{J}_s{}^{\pm} = \hat{J}_s{}^{\pm} R_z{}^{\beta} \tag{12-38}$$

and

$$R_\alpha{}^\pi \hat{J}_s{}^\pm = \hat{J}_s{}^\pm R_\alpha{}^\pi. \tag{12-39}$$

Using Eq. (11-41) for the symmetric top wavefunction $|J,0,0\rangle$ and the transformation properties of the Euler angle θ given in Table 12-1 we deduce that

$$R_z{}^\beta |J,0,0\rangle = |J,0,0\rangle \tag{12-40}$$

and

$$R_\alpha{}^\pi |J,0,0\rangle = (-1)^J |J,0,0\rangle. \tag{12-41}$$

Thus from Eqs. (11-52), (12-36), (12-38), and (12-40) we have

$$\begin{aligned} R_z{}^\beta |J,|k|,\pm|m|\rangle &= R_z{}^\beta N(\hat{J}_{\mathrm{m}}^-)^{|k|}(\hat{J}_s{}^\pm)^{|m|}|J,0,0\rangle \\ &= e^{+i|k|\beta}|J,|k|,\pm|m|\rangle. \end{aligned} \tag{12-42}$$

Similarly

$$R_z{}^\beta |J,-|k|,\pm|m|\rangle = e^{-i|k|\beta}|J,-|k|,\pm|m|\rangle. \tag{12-43}$$

Also from Eqs. (11-52), (12-37), (12-39), and (12-41) we have

$$\begin{aligned} R_\alpha{}^\pi |J,|k|,\pm|m|\rangle &= R_\alpha{}^\pi N(\hat{J}_{\mathrm{m}}^-)^{|k|}(\hat{J}_s{}^\pm)^{|m|}|J,0,0\rangle \\ &= (-1)^J e^{-i2|k|\alpha}|J,-|k|,\pm|m|\rangle \end{aligned} \tag{12-44}$$

and

$$R_\alpha{}^\pi |J,-|k|,\pm|m|\rangle = (-1)^J e^{i2|k|\alpha}|J,|k|,\pm|m|\rangle. \tag{12-45}$$

Summarizing these results we have

$$R_z{}^\beta |J,k,m\rangle = e^{ik\beta}|J,k,m\rangle \tag{12-46}$$

and

$$R_\alpha{}^\pi |J,k,m\rangle = (-1)^J e^{-2ik\alpha}|J,-k,m\rangle. \tag{12-47}$$

The $(2J+1)$ m-degeneracy of each (J,k) state can be neglected (unless an external field is applied). The transformation properties of symmetric top functions that have J half-integral are given in Eqs. (18-41) and (18-42).

The results in Eqs. (12-46) and (12-47) enable one to determine the transformation properties and symmetry of the rotational wavefunctions of any symmetric top molecule having J integral in its MS group using the equivalent rotations of the elements. We use the BF_3 and CH_3F molecules as examples below, and then we show how to deal with asymmetric top molecules.

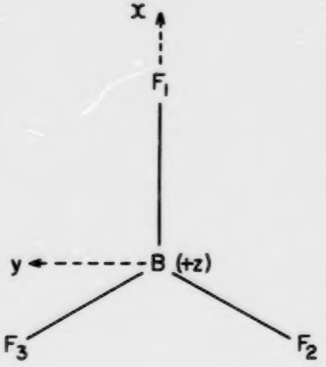

Fig. 12-6. The molecule fixed axes and nuclear labeling convention for the BF_3 molecule in its ground electronic state. The z axis is pointing up out of the page.

The BF_3 molecule, and the molecule fixed axis system used, is drawn in Fig. 12-6. Its MS group is $\boldsymbol{D}_{3h}(M)$. The character table of $\boldsymbol{D}_{3h}(M)$ and the equivalent rotations are given in Table A-10. Using Eqs. (12-40) and (12-41) we see that the representation generated by the function $|J,0,0\rangle$ is [where the operations are given in the same order as in Table A-10 for the group $\boldsymbol{D}_{3h}(M)$]

$$1, 1, (-1)^J, 1, 1, (-1)^J. \tag{12-48}$$

For the pair of functions $|J,K,m\rangle, |J,-K,m\rangle$ the representation generated is [using Eqs. (12-46) and (12-47)]

$$2, 2\cos(2\pi K/3), 0, 2(-1)^K, 2\cos(-\pi K/3), 0. \tag{12-49}$$

The representations in Eqs. (12-48) and (12-49) can be written in terms of the irreducible representations of $\boldsymbol{D}_{3h}(M)$ and these symmetry species, as a function of J and $K = |k|$, are collected in Table 12-5. The results for CH_3F (obtained using Table A-6) are also given in Table 12-5. It is necessary to multiply these species by $(2J+1)$ if one wishes to allow for the m-degeneracy.

To explain the way we determine the symmetry species of the rotational wavefunctions of an asymmetric top molecule, once we know the equivalent rotations of the MS group elements, we will use the H_2O molecule as an example. We will develop the *asymmetric top symmetry rule* which is used in Problem 12-2 for the CH_2O, C_2H_4 and trans $C_2H_2F_2$ molecules.

The rotational wavefunctions of the water molecule in a I^r basis are linear combinations of symmetric top rotational wavefunctions $|J,k_a,m\rangle$, and in a III^r basis they are linear combinations of $|J,k_c,m\rangle$ functions.[2] It will be instructive to classify both the $|J,k_a,m\rangle$ basis wavefunctions and the $|J,k_c,m\rangle$ basis wavefunctions in the MS group $\boldsymbol{C}_{2v}(M)$ (see Table A-5) and to consider the correlation of these symmetry labels. As a result we will be able to label by symmetry the asymmetric rotor wavefunctions and determine a general set of rules for enabling this to be done for any asymmetric top.

---

[2] The I^r and III^r conventions are explained in connection with Fig. 10-2 on page 210.

Table 12-5

Symmetry species of the rotational wavefunctions of BF_3 in the $\boldsymbol{D}_{3h}$(M) group, and of CH_3F in the $\boldsymbol{C}_{3v}$(M) group[a]

K	BF_3	K	CH_3F
0 J even	A_1'	0 J even	A_1
J odd	A_2'	J odd	A_2
$6n \pm 1$	E''	$3n \pm 1$	E
$6n \pm 2$	E'	$3n$	$A_1 \oplus A_2$
$6n \pm 3$	$A_1'' \oplus A_2''$		
$6n \pm 6$	$A_1' \oplus A_2'$		

[a] The $(2J+1)$ m-degeneracy is ignored. n is integral, and $K = |k|$.

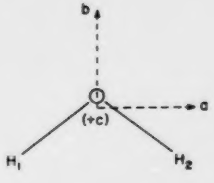

Fig. 12-7. The inertial axes for the water molecule labeled so that the moments of inertia are in the order $I_{aa} < I_{bb} < I_{cc}$.

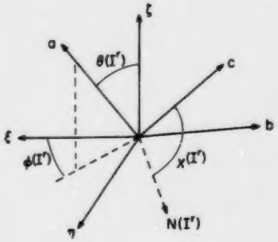

Fig. 12-8. The definition of the Euler angles using a type I^r convention, i.e., $abc \equiv zxy$.

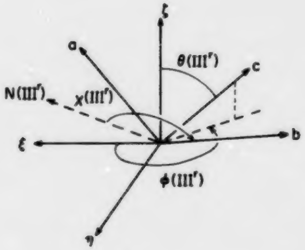

Fig. 12-9. The definition of the Euler angles using a type III^r convention, i.e., $abc \equiv xyz$.

The water molecule and its axis system are shown in Fig. 12-7. In a I^r representation the Euler angles are $\theta(I^r), \phi(I^r)$, and $\chi(I^r)$, and in a III^r representation they are $\theta(\text{III}^r)$, $\phi(\text{III}^r)$, and $\chi(\text{III}^r)$, as indicated in Figs. 12-8 and 12-9. The transformation properties of $\theta(\text{I}^r)$, $\phi(\text{I}^r)$, and $\chi(\text{I}^r)$, and those of $\theta(\text{III}^r)$, $\phi(\text{III}^r)$, and $\chi(\text{III}^r)$ are easily determined. The results are collected together in Table 12-6. These results can be obtained from the results in Table 12-1 once we have identified the equivalent rotations of each MS group element; these identifications are

$$(12):\quad R_b^{\pi},\quad E^*:\quad R_c^{\pi},\quad (12)^*:\quad R_a^{\pi}. \tag{12-50}$$

Thus, for example, $(12)^*$ rotates the molecule fixed axes through π radians about the a axis (R_a^{π}), and in a III^r basis ($abc \equiv xyz$) this is R_0^{π} in the notation of Table 12-1. From the results in Table 12-6, and using the results in Eqs. (12-46) and (12-47), we can obtain the representations of $C_{2v}(M)$ generated by the $|J, k_a, m\rangle$ and $|J, k_c, m\rangle$ functions. The results are given in Table 12-7. These results must be multiplied by $(2J+1)$ if we wish to allow for the m-degeneracy. To determine the symmetry species of the asymmetric rotor functions we can correlate between the K_a and K_c species labels given in Table 12-7, and the result is shown in Fig. 12-10. Alternately we could set up + and − combinations of $|J, K_a, m\rangle$ and $|J, -K_a, m\rangle$ functions and determine their transformation properties. The symmetry species for a rigid rotor state $J_{K_aK_c}$ depends only on the evenness or oddness of K_a and K_c, and the result is summarized in Table 12-8 where ee is any state $J_{K_aK_c}$ for which K_a and K_c are even (e), and eo is any state for which K_a is even (e) and K_c odd (o), etc.

Table 12-6

Transformation properties of the I^r and III^r Euler angles[a] for the H_2O molecule of Fig. (8-2) in the $C_{2v}(M)$ group[b]

E	(12)	E^*	$(12)^*$
Equiv. rot.	R_b^{π}	R_c^{π}	R_a^{π}
$\theta(\text{I}^r)$	$\pi - \theta(\text{I}^r)$	$\pi - \theta(\text{I}^r)$	$\theta(\text{I}^r)$
$\phi(\text{I}^r)$	$\phi(\text{I}^r) + \pi$	$\phi(\text{I}^r) + \pi$	$\phi(\text{I}^r)$
$\chi(\text{I}^r)$	$2\pi - \chi(\text{I}^r)$	$\pi - \chi(\text{I}^r)$	$\chi(\text{I}^r) + \pi$
$\theta(\text{III}^r)$	$\pi - \theta(\text{III}^r)$	$\theta(\text{III}^r)$	$\pi - \theta(\text{III}^r)$
$\phi(\text{III}^r)$	$\phi(\text{III}^r) + \pi$	$\phi(\text{III}^r)$	$\phi(\text{III}^r) + \pi$
$\chi(\text{III}^r)$	$\pi - \chi(\text{III}^r)$	$\chi(\text{III}^r) + \pi$	$2\pi - \chi(\text{III}^r)$

[a] See Figs. (12-8) and (12-9).

[b] See Table A-5.

From the correlation between the oblate and prolate rotor species given in Table 12-7 we can appreciate a simple way of determining the species of asymmetric rotor levels in the MS group. We first determine the equivalent rotation

Table 12-7

Representations of the $C_{2v}(M)$ group for H_2O generated by basis functions $|J, k_a, m\rangle$ and $|J, k_c, m\rangle$[a]

K_a		Γ_{rot}	K_c		Γ_{rot}
0	J even	A_1	0	J even	A_1
	J odd	B_1		J odd	B_2
odd		$A_2 \oplus B_2$	odd		$A_2 \oplus B_1$
even		$A_1 \oplus B_1$	even		$A_1 \oplus B_2$

[a] $K_a = |k_a|$, $K_c = |k_c|$.

of each MS group element (for an asymmetric top this can only be one of E, R_a^π, R_b^π, and R_c^π). We then use the ***asymmetric top symmetry rule*** which states that:

The ee functions will transform as the totally symmetric representation, the eo functions as the representation having +1 for R_a^π (and −1 for R_b^π and R_c^π), the oe functions as the representation having +1 for R_c^π (and −1 for R_a^π and R_b^π), and the oo functions as the representation having +1 under R_b^π (and −1 for R_a^π and R_c^π).

We will see in the subsection on the molecular rotation group [see Eq. (12-106) and the discussion following it on page 304] how this symmetry rule is related to the use of the molecular rotation group $\boldsymbol{D}_2$ for an asymmetric top molecule.

Problem 12-2. Classify the asymmetric rotor wavefunctions of formaldehyde (CH_2O), ethylene, and trans $C_2H_2F_2$ in their respective MS groups.

Answer. The formaldehyde molecule and its inertial axes are shown in Fig. 12-11. The MS group is the $\boldsymbol{C}_{2v}(M)$ group as for H_2O but since the *a* axis is the twofold symmetry axis of the molecule the identification of the equivalent rotations with the MS group elements is different from that given in Eq. (12-50) (or as given in Table A-5) and instead we have:

$$(12): \quad R_a^\pi, \quad E^*: \quad R_c^\pi, \quad (12)^*: \quad R_b^\pi. \tag{12-51}$$

Using the asymmetric top symmetry rule, the symmetry species of the asymmetric rotor states in the $\boldsymbol{C}_{2v}(M)$ group for formaldehyde are as given in Table 12-9.

The ethylene molecule and its inertial axes are shown in Fig. 12-12. The MS group, $\boldsymbol{D}_{2h}(M)$ is given in Table A-9. The equivalent rotations of the elements

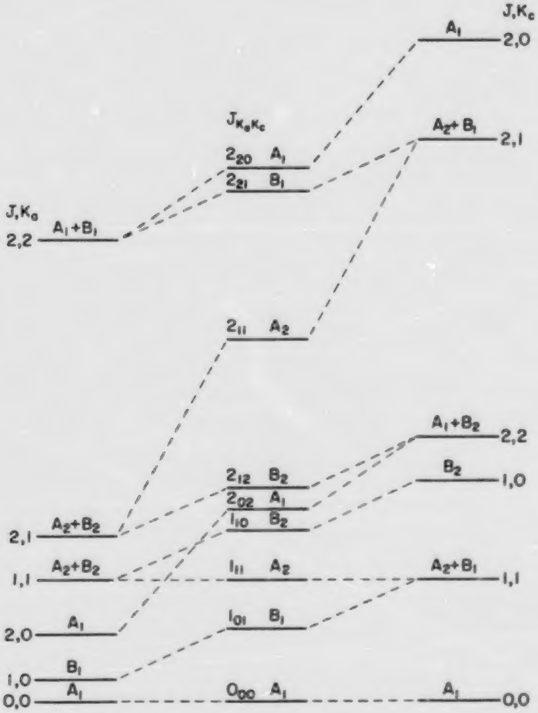
J,K_c
A_1
2,0
J_{K_aK_c}
2_{20} A_1
2_{21} B_1
A_2+B_1
2,1
J,K_a
A_1+B_1
2,2
2_{11} A_2
A_1+B_2
2,2
B_2
1,0
2_{12} B_2
2_{02} A_1
1_{10} B_2
2,1
A_2+B_2
1,1
A_2+B_2
1_{11} A_2
A_2+B_1
1,1
2,0
A_1
1_{01} B_1
1,0
B_1
0,0
A_1
0_{00} A_1
A_1
0,0

Fig. 12-10. The C_{2v}(M) symmetry labels for the asymmetric rotor energy levels of H_2O (center) and their correlation with the prolate rotor (left) and oblate rotor (right) levels.

Table 12-8

Symmetry species of $J_{K_a K_c}$ levels of H_2O in the C_{2v}(M) group

K_aK_c	Γ_{rot}	K_aK_c	Γ_{rot}
ee	A_1	oe	B_2
eo	B_1	oo	A_2

of the D_{2h}(M) group are

$$\begin{array}{rl} E \text{ and } (14)(23)(56)^* : & R^0, \\ (12)(34) \text{ and } (13)(24)(56)^* : & R_a{}^{\pi}, \\ (13)(24)(56) \text{ and } (12)(34)^* : & R_b{}^{\pi}, \\ (14)(23)(56) \text{ and } E^* : & R_c{}^{\pi}. \end{array} \tag{12-52}$$

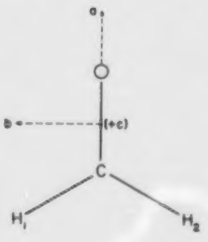

Fig. 12-11. The inertial axes of the formaldehyde molecule.

Table 12-9

Symmetry species of $J_{K_a K_c}$ levels of CH_2O in the $C_{2v}(M)$ group

K_aK_c	Γ_{rot}	K_aK_c	Γ_{rot}
ee	A_1	oe	B_2
eo	A_2	oo	B_1

The symmetries of the asymmetric top functions of ethylene are determined from the asymmetric top symmetry rule to be as given in Table 12-10.

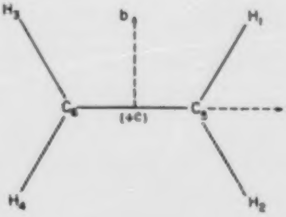

Fig. 12-12. The inertial axes of the ethylene molecule.

The principal axes of trans $C_2H_2F_2$ are located as shown in Fig. 12-13 and the MS group, $C_{2h}(M)$ is shown in Table A-8. The rotation of the axes caused by the elements of the $C_{2h}(M)$ group are

$$\begin{aligned} &E \text{ and } (12)(34)(56)^* : \quad R^0, \\ &(12)(34)(56) \text{ and } E^* : \quad R_c^{\pi}. \end{aligned} \tag{12-53}$$

The symmetries of the asymmetric top functions of trans $C_2H_2F_2$ are deduced from these results to be as given in Table 12-11. Notice that although the $C_{2h}(M)$ group has four irreducible representations there are only two possible species for the rotational wavefunctions. This is because the rotational

Table 12-10

Symmetry species of $J_{K_a K_c}$ levels of ethylene in the $\boldsymbol{D}_{2h}$(M) group

K_aK_c	Γ_{rot}	K_aK_c	Γ_{rot}
ee	A_g	oe	B_{3g}
eo	B_{1g}	oo	B_{2g}

Fig. 12-13. The inertial axes for trans $C_2H_2F_2$.

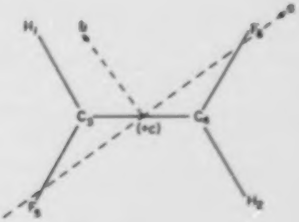

Table 12-11

Symmetry species of $J_{K_a K_c}$ levels of trans $C_2H_2F_2$ in the $\boldsymbol{C}_{2h}$(M) group

K_aK_c	Γ_{rot}	K_aK_c	Γ_{rot}
ee	A_g	oe	A_g
eo	B_g	oo	B_g

wavefunctions are invariant to the operation (12)(34)(56)*. Similarly for ethylene the rotational wavefunctions are invariant to the MS group operation (14)(23)(56)*. The reason for this is that these operations do not affect the orientation of the molecule fixed axes and do not change the Euler angles. Each of these operations has the same effect on the rovibronic coordinates as the operation *i* of the molecular point group, as is discussed in Chapter 4 [see Eq. (4-7) and the discussion following that equation].

The MS group of methane $\boldsymbol{T}_d$(M) (see Table A-14) involves rotations of the molecule about several axes, and for some of the operations of the group the Euler angle transformations are very complicated. For a given value of the *J* quantum number there are $(2J+1)^2$ states having $m, k = -J, -J+1, \ldots, +J$

Table 12-12

Symmetry species of rotational wavefunctions of methane in $\boldsymbol{T}_\mathrm{d}(\mathrm{M})$, and of SF_6 in $\boldsymbol{O}_\mathrm{h}(\mathrm{M})$, as a function of J^a

J	Γ_{rot}
$12n$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1$
$12n+1$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus F_1$
$12n+2$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus E \oplus F_2$
$12n+3$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_2 \oplus F_1 \oplus F_2$
$12n+4$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1 \oplus E \oplus F_1 \oplus F_2$
$12n+5$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus E \oplus 2F_1 \oplus F_2$
$12n+6$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1 \oplus A_2 \oplus E \oplus F_1 \oplus 2F_2$
$12n+7$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_2 \oplus E \oplus 2F_1 \oplus 2F_2$
$12n+8$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1 \oplus 2E \oplus 2F_1 \oplus 2F_2$
$12n+9$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1 \oplus A_2 \oplus E \oplus 3F_1 \oplus 2F_2$
$12n+10$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_1 \oplus A_2 \oplus 2E \oplus 2F_1 \oplus 3F_2$
$12n+11$	$n(A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2) \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2$

[a] n is integral. For the symmetry species of the rotational wavefunctions of SF_6 in $\boldsymbol{O}_\mathrm{h}(\mathrm{M})$ add a g to the subscripts.

all with the same energy in the rigid rotor approximation. This set of functions will transform as the representation $D^{(J)}$ of the group $\boldsymbol{K}$(mol). Using the correlation table of the group $\boldsymbol{K}$(mol) onto the group $\boldsymbol{T}_\mathrm{d}$ (see Appendix $\boldsymbol{B}$) we can reduce the representation $D^{(J)}$ and determine the symmetry species in $\boldsymbol{T}_\mathrm{d}(\mathrm{M})$ of each set of $(2J+1)^2$ functions $|J,k,m\rangle$ for a given value of J. The result is given in Table 12-12 where we have not included the m-degeneracy [to include the m-degeneracy it is necessary to multiply the species by $(2J+1)$]. The symmetry species of the rotational wavefunctions of SF_6 in $\boldsymbol{O}_\mathrm{h}(\mathrm{M})$ are given by the results in Table 12-12 by adding a g to the subscripts on the symmetry species. The symmetry species of the rotational wavefunctions of icosahedral molecules such as $B_{12}H_{12}{}^{2-}$, $C_{20}H_{20}$ and C_{60} in $\boldsymbol{I}_\mathrm{h}(\mathrm{M})$ are given in Harter and Weeks (1989). Because of the complicated Euler angle transformations to which some elements of the MS group give rise, it is not very easy to determine the transformation properties of individual $|J,k,m\rangle$ functions of a spherical top molecule in its MS group.

12.3 THE CLASSIFICATION OF THE VIBRATIONAL WAVEFUNCTIONS

To determine the symmetry species of the vibrational wavefunctions of a molecule in a particular electronic state we begin by determining the symmetry species of the normal coordinates (see Section 12.1.2). The vibrational wavefunction of a molecule in the harmonic oscillator approximation is the product of harmonic oscillator functions (one for each normal coordinate), and each harmonic oscillator function can be classified in the MS group, once we know the symmetry of the normal coordinate, by using the expressions given in Chapter 11 for the harmonic oscillator wavefunctions. The symmetry of the complete vibrational wavefunction is the product of the symmetries of the individual harmonic oscillator wavefunctions.

The harmonic oscillator wavefunction for a nondegenerate vibration when the vibrational quantum number v is zero is given by [see Eq. (11-101)]

$$\Phi_0 = (\gamma/\pi)^{1/4}\exp(-\gamma Q^2/2), \tag{12-54}$$

where $\gamma = \lambda^{1/2}/\hbar$. The potential energy in the harmonic oscillator approximation is $(\hbar^2\gamma^2/2)Q^2$ and this must be totally symmetric in the MS group since the MS group is a symmetry group of the Hamiltonian. As a result Q^2, and hence the $v = 0$ function Φ_0, must be totally symmetric in the MS group. For a nondegenerate normal coordinate the excited state harmonic oscillator wavefunction Φ_v, with vibrational quantum number v, is given by [see Eq. (11-107)]

$$\Phi_v = N_v'[(-i\hbar/\sqrt{2})\partial/\partial Q + (i\hbar\gamma\sqrt{2})Q]^v\Phi_0 = N_v'(\hat{R}^+)^v\Phi_0, \tag{12-55}$$

where N_v' is a normalization constant. If the normal coordinate Q transforms according to the one-dimensional representation, $\Gamma^{(i)}$, say, of the MS group, the ladder operator $\hat{R}^+$ will also transform according to the representation $\Gamma^{(i)}$. Since $\hat{R}^+$ transforms as $\Gamma^{(i)}$ then $(\hat{R}^+)^v$ and (since Φ_0 is totally symmetric) Φ_v will transform as the product $\Gamma^{(i)} \otimes \Gamma^{(i)} \otimes \Gamma^{(i)} \otimes \cdots$ taken v times; for v even this is the totally symmetric representation and for v odd this is $\Gamma^{(i)}$.

A pair of doubly degenerate normal coordinates Q_a and Q_b (which are such that $\gamma_a = \gamma_b = \gamma$ in the potential function) will form the basis for a two-dimensional irreducible representation, $\Gamma^{(j)}$, say, of the MS group. From the discussion in Chapter 11 [see Eqs. (11-165) and (11-166)] we deduce that the vibrational wavefunction for the lowest level ($v = l = 0$) is given by

$$\Psi_{0,0} = (\gamma/\pi)^{1/2}\exp[-(\gamma Q^2/2)], \tag{12-56}$$

and that the excited state vibrational wavefunctions are given by

$$\Psi_{v,l} = N'_{v,l}(\hat{R}^{+(-)})^{(v-l)/2}(\hat{R}^{+(+)})^{(v+l)/2}\Psi_{0,0}, \tag{12-57}$$

where the ladder operators $\hat{R}^{\pm(\pm)}$ are defined in Eq. (11-157) and $Q^2 = Q_a{}^2 + Q_b{}^2$. From the invariance of the potential function term $(\hbar^2\gamma^2/2)Q^2$ we deduce that $\Psi_{0,0}$ is totally symmetric in the MS group. Given that $\Psi_{0,0}$ is totally symmetric then, from Eq. (12-57), we see that the $(v+1)$ degenerate functions $\Psi_{v,l}$, where $l = v, v-2, v-4, \ldots, -v$, transform in the same way as the $(v+1)$ operators

$$(\hat{R}^{+(+)})^v, (\hat{R}^{+(-)})(\hat{R}^{+(+)})^{v-1}, (\hat{R}^{+(-)})^2(\hat{R}^{+(+)})^{v-2}, \ldots, (\hat{R}^{+(-)})^v, \tag{12-58}$$

i.e., as the symmetric vth power of the two-dimensional representation generated by the pair of ladder operators $(\hat{R}^{+(+)}, \hat{R}^{+(-)})$ [see Eq. (6-121)]. From

Eqs. (11-155)-(11-157) we see that $(\hat{R}^{+(+)} + \hat{R}^{+(-)})$ transforms as Q_a and that $(\hat{R}^{+(+)} - \hat{R}^{+(-)})$ transforms as Q_b, so that $(\hat{R}^{+(+)}, \hat{R}^{+(-)})$ transforms like (Q_a, Q_b), i.e., as $\Gamma^{(j)}$. Thus the $(v+1)$ degenerate functions $\Psi_{v,l}$ transform as the symmetric vth power of the normal coordinate species $\Gamma^{(j)}$; this is written as $[\Gamma^{(j)}]^v$ [see Eq. (6-121)].

For a triply degenerate vibration (v_a, v_b, v_c) with coordinates Q_a, Q_b, and Q_c, and $\gamma_a = \gamma_b = \gamma_c = \gamma$, each level has an energy of

$$E(v_a, v_b, v_c) = \left[v + \frac{3}{2}\right]\hbar^2\gamma, \tag{12-59}$$

where $v = (v_a + v_b + v_c)$, and each level has a degeneracy of $(v+1)(v+2)/2$ as

$$(v_a, v_b, v_c) = (v,0,0), (v-1,1,0), (v-1,0,1), \ldots, (0,0,v).$$

The $v = 0$ function is totally symmetric and the three $v = 1$ functions transform as the normal coordinates (Q_a, Q_b, Q_c), i.e., as the three-dimensional irreducible representation, F, say, of the MS group. For v greater than one, the symmetry of the $(v+1)(v+2)/2$ independent functions is the symmetric vth power of the normal coordinate representation and this is written $[F]^v$. For a three-dimensional species F the character under the operation R in the representation $[F]^v$ is given by [see Section 7-3 in Wilson, Decius, and Cross (1955)]

$$\chi^{[F]^v}[R] = \frac{1}{3}\Big[2\chi^F[R]\chi^{[F]^{v-1}}[R] + \frac{1}{2}\Big\{\chi^F[R^2] \\ - (\chi^F[R])^2\Big\}\chi^{[F]^{v-2}}[R] + \chi^F[R^v]\Big]. \tag{12-60}$$

This is an extension of Eq. (6-121) to a three-dimensional representation.

The methane molecule provides an instructive example [see Eqs. (12-30) and (12-31)]. A vibrational energy level of methane is described by the values of the four quantum numbers v_1, v_2, v_3, and v_4, and we will determine the symmetry of the vibrational state $(v_1, v_2, v_3, v_4) = (3,2,1,2)$ in the $\boldsymbol{T}_\mathrm{d}(\mathrm{M})$ group (see Table A-14). To do this we first determine the symmetry species of the vibrational wavefunctions of each of the four modes and then multiply these species together. For the v_1 mode of species A_1 we have $v_1 = 3$ and

$$\Gamma(\Phi_{v_1=3}) = A_1 \otimes A_1 \otimes A_1 = A_1. \tag{12-61}$$

For the v_2 mode we have [using Eq. (6-119) for $[E]^2 = [E \otimes E]$]

$$\Gamma(\Phi_{v_2=2}) = [E]^2 = A_1 \oplus E, \tag{12-62}$$

and similarly

$$\Gamma(\Phi_{v_3=1}) = F_2, \tag{12-63}$$

and [using Eq. (12-60)]

$$\Gamma(\Phi_{v_4=2}) = [F_2]^2 = A_1 \oplus E \oplus F_2. \tag{12-64}$$

Thus

$$\begin{aligned}\Gamma(\Phi_{v_1=3}\Phi_{v_2=2}\Phi_{v_3=1}\Phi_{v_4=2}) &= A_1 \otimes (A_1 \oplus E) \otimes F_2 \otimes (A_1 \oplus E \oplus F_2)\\ &= 2A_1 \oplus A_2 \oplus 3E \oplus 7F_1 \oplus 8F_2. \end{aligned} \tag{12-65}$$

In the general case of a molecule with normal coordinates of species $\Gamma^{(1)}, \Gamma^{(2)}, \ldots, \Gamma^{(f)}$ in a vibrational state with quantum numbers $v_1, v_2, \ldots, v_f$ the species of the vibrational wavefunctions is

$$\Gamma(v_1, v_2, \ldots, v_f) = [\Gamma^{(1)}]^{v_1} \otimes [\Gamma^{(2)}]^{v_2} \otimes \cdots \otimes [\Gamma^{(f)}]^{v_f}, \tag{12-66}$$

where $[\ ]^v$ is the symmetric vth product for a degenerate species and the ordinary vth product for a nondegenerate species.

12.4 THE CLASSIFICATION OF ROTATION-VIBRATION WAVEFUNCTIONS

As we will see in Chapter 13 centrifugal distortion and Coriolis coupling interactions in a symmetric top molecule can mix states of different K value [see, for example, Eqs. (13-76) and (13-79)]. If the interaction is strong it spoils the usefulness of K as a near quantum number. However, for symmetric top molecules we can use symmetry to define related "good" rotation-vibration quantum numbers g_{rv}, η, and τ. Similar vibrational, vibronic and rovibronic quantum numbers g_{v}, g_{ve}, and g can also be defined [see Hougen (1962c), Mills (1964a) and Hegelund, Rasmussen, and Brodersen (1973)]. In order to understand how these quantum numbers are defined we introduce the concept of ***generating operations*** of a group.

The MS group $C_{3v}(\mathrm{M})$ [Table A-6] contains the six operations

$$C_{3v}(\mathrm{M}) = \{E, (123), (132), (12)^*, (13)^*, (23)^*\}. \tag{12-67}$$

The following relations hold [see Table 1-1]

$$\begin{aligned} E &= (123)(123)(123) = (23)^*(23)^*,\\ (132) &= (123)(123),\\ (12)^* &= (23)^*(123)(123),\\ (13)^* &= (23)^*(123). \end{aligned} \tag{12-68}$$

Thus we can express *all* $C_{3v}(\mathrm{M})$ operations in terms of (123) and $(23)^*$; these two operations are ***generating operations***, or ***group generators***, for $C_{3v}(\mathrm{M})$. The generators of a group are a set of elements of the group which is such that every element of the group can be expressed as a finite product of powers of elements of the set. If we want to symmetry classify an operator (or a function) in $\boldsymbol{C}_{3v}$(M), it is sufficient to know how the operator (or function) transforms under the generating operations (123) and (23)*, since we can use Eq. (12-68) to construct the transformation properties under all other operations.

For the most important symmetric top point groups,[3] $\boldsymbol{C}_{nv}$ ($n \geq 3$), $\boldsymbol{D}_{nh}$ ($n \geq 3$), and $\boldsymbol{D}_{nd}$ ($n \geq 2$), we can express all group operations in terms of at most three generating operations R_+, R'_+, and R_-. Table 12-13 summarizes convenient sets of generating operations for each of these groups. For a rigid symmetric top molecule, the molecular symmetry group and the molecular point group are isomorphic. Consequently, for such a molecule the operations of the molecular symmetry group can also be expressed in terms of at most three generating operations that are the MS group partners of the point group operations given in Table 12-13. In the MS group, the partner operation of the rotation C_n is a permutation for which the equivalent rotation is of type R_z^{β} and it is that operation for which β ($= 2\pi/n$) has the smallest value ($\beta_{\min}$) (or alternatively involves the largest value of n; the order of the primary axis of symmetry). For example, in the case of the $\boldsymbol{C}_{3v}$(M) molecule CH_3F described by Table A-6, the point group operation C_n corresponds to the MS group operation (123) as given in the example above. If the molecule under study has one set of n identical nuclei arranged symmetrically around the n-fold rotation axis in the equilibrium configuration of the molecule, then these nuclei can be labeled such that the MS group partner operation of C_n is the cyclic permutation $(123\ldots n)$. The groups $\boldsymbol{D}_{nd}$ where n is even and $\boldsymbol{S}_m$ where $m/2$ is even are exceptions in that the MS group partner of the operation R_+ is not a pure permutation; it is that permutation-inversion for which the equivalent rotation is R_z^{β} with the smallest positive β value. The MS group partner of the inversion i is the operation O_i given by Eq. (4-7). The partners of the other point group operations in Table 12-13 will vary, and in the character tables of Appendix ***A*** the MS group–point group partners are indicated. For CH_3F [Table A-6], the point group operation σ_{xz} corresponds to the MS group operation (23)*. In the case of the $\boldsymbol{D}_{3h}$(M) molecule BF_3 described by Table A-10, the point group operation σ_h corresponds to the MS group operation E^*, and the point group operation C_{2x} corresponds to the MS group operation (23).

At the end of Section 12.1.2 we showed that it is necessary to choose a convention for the MS group transformation properties of the normal coordinates belonging to degenerate irreducible representations. We use the convention introduced by di Lauro and Mills (1966) which is conveniently expressed in terms of the generating operations in Table 12-13. For groups that have C_n as a generating operation we require the normal coordinates (Q_{ta}, Q_{tb}) to transform as

$$C_n(Q_{ta} + iQ_{tb}) = \exp\left[-i\frac{2\pi}{n}r_t\right](Q_{ta} + iQ_{tb}) \tag{12-69}$$

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[3] **Point groups having separably degenerate irreducible representations are not included here. These are the groups $\boldsymbol{C}_n$ and $\boldsymbol{C}_{nh}$ ($n = 3, 4, 5, \ldots$), $\boldsymbol{S}_n$ ($n = 4, 6, 8, \ldots$) and $\boldsymbol{T}$.**

Table 12-13

Generating operations for common point groups of symmetric tops

Molecular point group	R_+	R'_+	R_-
$\boldsymbol{C}_{n\mathrm{v}}$ ($n \geq 3$)	C_n		σ_{xz}
$\boldsymbol{D}_{n\mathrm{h}}$ ($n \geq 3$; n odd)	C_n	σ_h	C_{2x}
$\boldsymbol{D}_{n\mathrm{h}}$ ($n \geq 4$; n even)	C_n	i	C_{2x}
$\boldsymbol{D}_{n\mathrm{d}}$ ($n \geq 3$; n odd)	C_n	i	C_{2x}
$\boldsymbol{D}_{(n/2)\mathrm{d}}$ ($n/2 \geq 2$; $n/2$ even)	S_n		C_{2x}

The group operations are described by means of a right-handed axis system xyz. The z axis is the n-fold rotation axis. C_n is a rotation through $2\pi/n$ about the z axis, C_{2x} is a rotation through π about the x axis, σ_{xz} is a reflection in the xz plane, σ_h is a reflection in the xy plane, i is a rotation through π about the z axis combined with a reflection in the xy plane, and S_n is a rotation through $2\pi/n$ about the z axis combined with a reflection in the xy plane.

under C_n or, equivalently, under the MS group partner of C_n. In Eq. (12-69) $r_t = 1, 2, 3, \ldots$ as (Q_{ta}, Q_{tb}) spans E_1, E_2, E_3, ... [i.e., r_t is defined so that the character under C_n of the irreducible representation spanned by (Q_{ta}, Q_{tb}) is $2\cos(2\pi r_t/n)$]. For groups with S_n as a generating operation we require that

$$S_n(Q_{ta} + iQ_{tb}) = \exp\left[-i\frac{2\pi}{n}r_t\right](Q_{ta} + iQ_{tb}). \tag{12-70}$$

If C_{2x} is a generating operation then

$$C_{2x}(Q_{ta} + iQ_{tb}) = Q_{ta} - iQ_{tb}, \tag{12-71}$$

and if σ_{xz} is a generating operation then

$$\sigma_{xz}(Q_{ta} + iQ_{tb}) = Q_{ta} - iQ_{tb}. \tag{12-72}$$

It is not necessary to specify a convention for the transformation of (Q_{ta}, Q_{tb}) under the generating operations i or σ_h. The normal coordinates will be invariant under i (σ_h), or they will change sign, depending on whether their irreducible representation is of type g (′) or u (″). As mentioned above the convention adopted here will cause normal coordinates (Q_{ta}, Q_{tb}) belonging to irreducible representations E_1 or E to transform as (T_x, T_y).

Having defined the generating operations R_+, R'_+, and R_- in Table 12-13 we need a general expression for the symmetric top rotation-vibration basis wavefunctions in order to express the transformation properties under these operations. In a non-degenerate electronic state, we determine the eigenvalues and eigenfunctions of the rotation-vibration Hamiltonian by diagonalizing it in a basis of functions

$$\Phi_{\rm rv}^{(V,L,J,k,m)} = |v_1\rangle\,|v_2\rangle \ldots |v_q\rangle\,|v_{q+1}, l_{q+1}\rangle\,|v_{q+2}, l_{q+2}\rangle \ldots |J,k,m\rangle\,. \qquad (12\text{-}73)$$

The function $\Phi_{\rm rv}^{(V,L,J,k,m)}$ is a product of harmonic oscillator functions (where the vibrational modes ν_1 to ν_q are assumed to be non-degenerate, so that they are described by a v quantum number only, whereas the remaining modes ν_{q+1}, $\nu_{q+2}, \ldots$ are doubly degenerate, so that each of them is described by a v and an l quantum number) and the symmetric top rotational wavefunction given by Eq. (11-52). In labeling the function $\Phi_{\rm rv}^{(V,L,J,k,m)}$, we use V as a shorthand notation for all v quantum numbers $(v_1, v_2, v_3, \ldots)$ and L as a shorthand notation for all l quantum numbers $(l_{q+1}, l_{q+2}, \ldots)$.

It can be shown [see Hougen (1962c), Mills (1964a), and Hegelund, Rasmussen, and Brodersen (1973)] that the transformation properties of the functions $\Phi_{\rm rv}^{(V,L,J,k,m)}$ under the generating operations R_+, R'_+, and R_- in the MS groups are

$$R_+\,\Phi_{\rm rv}^{(V,L,J,k,m)} = \exp\left[-i\,\frac{2\pi}{n}\,g_{\rm rv}\right]\,\Phi_{\rm rv}^{(V,L,J,k,m)}, \qquad (12\text{-}74)$$

$$R'_+\,\Phi_{\rm rv}^{(V,L,J,k,m)} = (-1)^{\eta}\,\Phi_{\rm rv}^{(V,L,J,k,m)}, \qquad (12\text{-}75)$$

and

$$R_-\,\Phi_{\rm rv}^{(V,L,J,k,m)} = (-1)^{\rho}\,\Phi_{\rm rv}^{(V,-L,J,-k,m)}. \qquad (12\text{-}76)$$

In Eq. (12-76), the function $\Phi_{\rm rv}^{(V,-L,J,-k,m)}$ is obtained from $\Phi_{\rm rv}^{(V,L,J,k,m)}$ by simultaneously changing the signs of all the l quantum numbers and the k quantum number. It is assumed here that the relative phases of the symmetric top functions $|J,k,m\rangle$ are chosen so that Eq. (11-51) is fulfilled, and that the relative phases of the two-dimensional (isotropic) harmonic oscillator eigenfunctions $|v_i, l_i\rangle$ are chosen in accord with Table 11-3. The quantities $g_{\rm rv}$, η, and ρ defining the transformation properties are given in Table 12-14.

Equations (12-74)-(12-76) show that the two basis functions $\Phi_{\rm rv}^{(V,L,J,k,m)}$ and $\Phi_{\rm rv}^{(V,-L,J,-k,m)}$ transform according to a two-dimensional representation with the character

$$\exp\left[-i\,\frac{2\pi}{n}\,g_{\rm rv}\right] + \exp\left[i\,\frac{2\pi}{n}\,g_{\rm rv}\right] = 2\cos\left[\frac{2\pi}{n}\,g_{\rm rv}\right] \qquad (12\text{-}77)$$

under the R_+ operation. From the character tables in Appendix ***A***, we can distinguish two types of basis function that we call Type I and Type II. The type depends on the value of $g_{\rm rv}$ as follows:

Table 12-14

The definitions of the quantum numbers g_{rv}, η, and ρ, that give the transformation properties of the symmetric top rotation-vibration basis functions

C_{nv} ($n \geq 3$; n odd)	$g_{\mathrm{rv}} = -k + \sum r_j l_j + nt$
	$\rho = J + k + \sum v_{A_2} + 2t$
C_{nv} ($n \geq 4$; n even)	$g_{\mathrm{rv}} = -k + \sum r_j l_j - (n/2) \sum v_B + nt$
	$\rho = J + k + \sum v_{A_2} + \sum v_{B_2} + 2t$
D_{nh} ($n \geq 3$; n odd)	$g_{\mathrm{rv}} = -k + \sum r_j l_j + nt$
	$\eta = k + \sum v^{('')} + 2t$
	$\rho = J + \sum v_{A_2} + 2t$
D_{nh} ($n \geq 4$; n even)	$g_{\mathrm{rv}} = -k + \sum r_j l_j - (n/2) \sum v_B + nt$
	$\eta = \sum v_u + 2t$
	$\rho = J + \sum v_{A_2} + \sum v_{B_2} + 2t$
D_{nd} ($n \geq 3$; n odd)	$g_{\mathrm{rv}} = -k + \sum r_j l_j + nt$
	$\eta = \sum v_u + 2t$
	$\rho = J + \sum v_{A_2} + 2t$
$D_{(n/2)d}$ ($n/2 \geq 2$; $n/2$ even)	$g_{\mathrm{rv}} = -k + \sum r_j l_j - (n/2)[\sum v_B + k] + nt$
	$\rho = J + \sum v_{A_2} + \sum v_{B_2} + 2t$

The sum $\sum_j r_j l_j$ in the definition of g_{rv} runs over all degenerate normal modes of the molecule in question with r_j as the numerical index on the symmetry symbol E_{r_j} spanned by the j'th normal vibration. The irreducible representation E_{r_j} has the character $2\cos(2\pi r_j/n)$ under the operation C_n. For point groups with $n \leq 4$ no numerical indices occur and all $r_j = 1$. The summations $\sum v_B$, $\sum v_{A_2}$, and $\sum v_{B_2}$ represent sums over the v quantum numbers belonging to non-degenerate normal modes with symmetries B, A_2, and B_2, respectively. The summations $\sum v_u$ and $\sum v^{('')}$, represent sums over the v quantum numbers belonging to non-degenerate or degenerate normal modes with symmetries of type u or $''$, respectively. The quantity t is an integer determined independently for the quantum numbers g_{rv}, η, and ρ, so that the quantum numbers have values that satisfy $-\frac{n}{2} < g_{\mathrm{rv}} \leq \frac{n}{2}$, $\eta = 0$ or 1 and $\rho = 0$ or 1.

I. If $g_{\mathrm{rv}} \neq 0$ and $g_{\mathrm{rv}} \neq \frac{n}{2}$, the basis functions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}$ and $\Phi_{\mathrm{rv}}^{(V,-L,J,-k,m)}$ transform according to an irreducible, doubly degenerate representation $E_{|g_{\mathrm{rv}}|}$. No further symmetrization of the basis functions is possible. In this case, we refer to the functions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}$ and $\Phi_{\mathrm{rv}}^{(V,-L,J,-k,m)}$ as Type I basis functions.

II. If $g_{\mathrm{rv}} = 0$, the basis functions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}$ and $\Phi_{\mathrm{rv}}^{(V,-L,J,-k,m)}$ transform according to a reducible two-dimensional representation $A_1 + A_2$. If $g_{\mathrm{rv}} = \frac{n}{2}$, they transform according to $B_1 + B_2$. In both cases, it is easy to verify that the new basis functions

$$\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)} = \frac{1}{\sqrt{2}} \left[\Phi_{\mathrm{rv}}^{(V,L,J,k,m)} + (-1)^{\rho+\tau} \Phi_{\mathrm{rv}}^{(V,-L,J,-k,m)}\right], \qquad (12\text{-}78)$$

where $\tau = 0$ or 1, have the following transformation properties

$$R_+ \Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)} = \exp\left[-i\,\frac{2\pi}{n}\,g_{\mathrm{rv}}\right] \Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}, \qquad (12\text{-}79)$$

$$R'_+ \Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)} = (-1)^{\eta} \Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}, \qquad (12\text{-}80)$$

and

$$R_- \Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)} = (-1)^{\tau} \Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}. \qquad (12\text{-}81)$$

Hence the new basis functions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}$ transform according to nondegenerate irreducible representations A_1, A_2, B_1, or B_2 in the MS group. We refer to them as Type II basis functions. A special case of a Type II basis function occurs when $k = 0$ and all $l_j = 0$. We define the corresponding symmetrized basis function as

$$\Phi_{\mathrm{rv}}^{(V,0,J,0,m,\tau)} = \Phi_{\mathrm{rv}}^{(V,0,J,0,m)} \qquad (12\text{-}82)$$

where, by definition, $\tau = \rho$. The basis function has transformation properties given by Eqs. (12-79)-(12-81).

We can also define [Hougen (1962c)] the related vibrational, vibronic and rovibronic quantum numbers g_{v}, g_{ve} and g using

$$R_+ \psi_{\mathrm{v}} = \exp\left[-i\frac{2\pi}{n}g_{\mathrm{v}}\right] \psi_{\mathrm{v}}, \qquad (12\text{-}83)$$

$$R_+ \psi_{\mathrm{ve}} = \exp\left[-i\frac{2\pi}{n}g_{\mathrm{ve}}\right] \psi_{\mathrm{ve}}, \qquad (12\text{-}84)$$

$$R_+ \psi_{\mathrm{rve}} = \exp\left[-i\frac{2\pi}{n}g\right] \psi_{\mathrm{rve}}. \qquad (12\text{-}85)$$

where $-\frac{n}{2} < g_{\mathrm{v}}, g_{\mathrm{ve}}, g \leq \frac{n}{2}$. From these definitions we obtain relations such as

$$g_{\mathrm{v}} = g_{\mathrm{rv}} + k + nt, \qquad (12\text{-}86)$$

$$g_{\mathrm{ve}} = g_{\mathrm{rve}} + k + nt. \qquad (12\text{-}87)$$

For CH_3F we have, for example,

$$g_{\mathrm{v}} = l_4 + l_5 + l_6 + 3t, \qquad (12\text{-}88)$$

where the integer t is determined so that $g_{\mathrm{v}} = -1$, 0, or 1.

We introduce the unsigned quantum numbers, for labeling energy levels,

$$G = |g|, \qquad G_{\mathrm{rv}} = |g_{\mathrm{rv}}|, \qquad G_{\mathrm{ve}} = |g_{\mathrm{ve}}|, \qquad \text{and} \qquad G_{\mathrm{v}} = |g_{\mathrm{v}}|.$$

Selection rules for rovibronic, vibronic, and rotation-vibration perturbations can be formulated using these quantum numbers. The quantum numbers (g_{rv}, η, τ), g, g_{ve}, and g_{v} contain no more information than the MS symmetry labels Γ_{rv}, Γ_{rve}, Γ_{ve}, and Γ_{vib}, respectively, but they are useful, for example when the selection rules derived from the MS group symmetry are to be incorporated in a computer program for simulating spectra. They are also useful in defining the $(\pm l)$ quantum number label. The $(\pm l)$ quantum number label is itself of particular use in discussing optical selection rules in symmetric tops when degenerate vibrational or vibronic states are involved. However, the definition of this label requires knowledge of the Coriolis coupling interaction for a symmetric top, and so we postpone the discussion of it until Section 13.2.2.

12.5 THE CLASSIFICATION OF THE ELECTRONIC WAVEFUNCTIONS

12.5.1 The classification of molecular orbitals

An electronic wavefunction $\Phi_{\mathrm{elec}}^{(e,S,m_S)}$ [see page 195] of a molecule, obtained in an SCF-CI calculation, can be written as a superposition of single configuration wavefunctions $\Phi_{\mathrm{elec}}^{\mathrm{SCF},q}$ [see Eq. (9-83)], each of which is a Slater determinant [Eq. (9-68)]. In the superposition given by Eq. (9-83), all the Slater determinants will transform according to the same irreducible representation of the MS group; this is a consequence of the vanishing integral rule [Eq. (6-140)] in conjunction with the fact that the wavefunction $\Phi_{\mathrm{elec}}^{(e,S,m_S)}$ is obtained by diagonalization of a matrix representation of the electronic Hamiltonian in the basis of $\Phi_{\mathrm{elec}}^{\mathrm{SCF},q}$ functions. Each Slater determinant $\Phi_{\mathrm{elec}}^{\mathrm{SCF},q}$ is the sum of $n!$ terms [n is the number of electrons in the molecule], and each of these terms is a product of n molecular orbitals

$$\phi_1(\boldsymbol{r}_{i_1})\phi_2(\boldsymbol{r}_{i_2})\cdots\phi_n(\boldsymbol{r}_{i_n}), \tag{12-89}$$

multiplied by n spin functions, where each spin function is either $\alpha(\sigma)$ or $\beta(\sigma)$. As discussed in Chapter 9, an orbital can occur at most twice in the product given in Eq. (12-89). The sequence of indices $i_1 i_2 \ldots i_n$ in the product is a permutation of the numbers $123\ldots n$, and the $n!$ orbital products which enter into a Slater determinant correspond to the $n!$ possible permutations of this kind; the MO products occurring in a given Slater determinant differ only in the labeling of the electrons. Thus, all these MO products have the same symmetry in the MS group.

When we know the irreducible representations generated by the Slater determinants $\Phi_{\mathrm{elec}}^{\mathrm{SCF},q}$ in the MS group, we immediately obtain the symmetries of the electronic wavefunctions $\Phi_{\mathrm{elec}}^{(e,S,m_S)}$ since these functions are expressed in terms of the Slater determinants by Eq. (9-83). The first step towards classifying a Slater determinant is to determine the common symmetry of the $n!$ MO products [Eq. (12-89)] contained in it. In the remainder of this section, we explain how to do this.

Note that the nuclear spin statistical weights of the rotational levels of a state depend on the electronic symmetry (as well as on the rotational and vibrational symmetry) and the relative intensities of the rotational lines in a spectrum depend on the statistical weights. Thus the experimental determination of these relative intensities can sometimes enable the symmetry of the lowest electronic state to be determined [see, for example, Carlotti, Johns, and Trombetti (1974)].

The molecular orbital functions $\phi_k(\boldsymbol{r})$ can be written as linear combinations of atomic orbital basis functions [Eq. (9-69)]. The symmetry of the MO product in Eq. (12-89) depends on the symmetries of the molecular orbitals $\phi_k(\boldsymbol{r})$ and these symmetries, in turn, can be obtained from the transformation properties of the atomic orbitals. Under the effect of an element of the MS group the molecule fixed (x, y, z) axes are rotated and the nuclear labels on the atomic orbitals are permuted. We will use the water molecule as a convenient example to show how the rotation of the (x, y, z) axes and the permutation of the nuclear labels affect the transformation properties of the atomic orbitals.

For the water molecule we consider molecular orbitals constructed from the following limited set of atomic orbitals centered on the oxygen nucleus, 1s(O), 2s(O), $2p_x$(O), $2p_y$(O), $2p_z$(O), together with the atomic orbitals $1s(H_1)$ and $1s(H_2)$ centered on the protons. The effect of the MS group operation (12) is shown in Fig. 12-14 and we see that

$$(12)2p_z(O) = -2p_z(O) \tag{12-90}$$

since although the electrons are unaffected by (12) the molecule fixed z axis is reversed. Also the (12) operation exchanges the the atomic orbitals $1s(H_1)$ and $1s(H_2)$ centered on the protons. We determine that the following combinations of atomic orbitals transform irreducibly:

$$\begin{aligned} A_1 &: \quad 1s(O),\ 2s(O),\ 2p_x(O),\ [1s(H_2) + 1s(H_1)], \\ B_1 &: \quad 2p_y(O), \\ B_2 &: \quad 2p_z(O),\ [1s(H_2) - 1s(H_1)]. \end{aligned} \tag{12-91}$$

These symmetry adapted combinations of atomic orbitals are called *symmetry orbitals* (SO) and MO's written as LCAO's [see Eq. (9-69)] can only consist of one symmetry type of SO as a result of the vanishing integral rule [Eq. (6-140)].

To determine how many orbitals of a given symmetry type are occupied, we argue as follows. The lowest lying MO will obviously be largely a 1s orbital on the oxygen nucleus, $(1a_1) = 1s(O)$. The two SO's of B_2 symmetry will form a bonding and an antibonding pair of MO's qualitatively given by

$$(1b_2) = 2p_z(O) + [1s(H_2) - 1s(H_1)] \tag{12-92}$$

and

$$(1b_2^*) = 2p_z(O) - [1s(H_2) - 1s(H_1)].$$

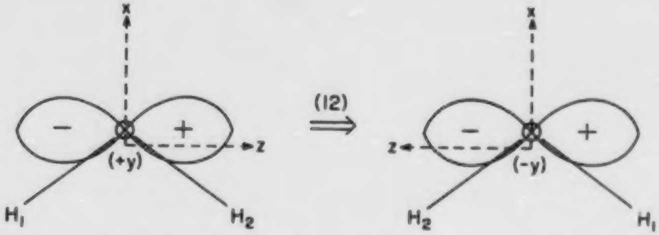

Fig. 12-14. The effect of the operation (12) for the water molecule witn the atomic orbital $2p_z(O)$ marked.

The $2s(O)$ and $2p_x(O)$ orbitals will each similarly form bonding and antibonding MO's with the $[1s(H_2) + 1s(H_1)]$ SO; the bonding orbitals are qualitatively given by

$$(2a_1) = 2s(O) + [1s(H_2) + 1s(H_1)] \tag{12-93}$$

and

$$(3a_1) = 2p_x(O) + [1s(H_2) + 1s(H_1)].$$

Finally the $2p_y(O)$ orbital will give a nonbonding orbital of symmetry B_1:

$$(1b_1) = 2p_y(O). \tag{12-94}$$

Filling the bonding and nonbonding MO's we obtain the electronic configuration of the ground state of H_2O (called the $\tilde{X}$ state) as

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2. \tag{12-95}$$

The orbitals are written in order of increasing energy and the symmetry of the MO product

$$\phi_{1a_1}(\boldsymbol{r}_1)\,\phi_{1a_1}(\boldsymbol{r}_2)\,\phi_{2a_1}(\boldsymbol{r}_3)\,\phi_{2a_1}(\boldsymbol{r}_4)\,\phi_{1b_2}(\boldsymbol{r}_5) \times \phi_{1b_2}(\boldsymbol{r}_6)\,\phi_{3a_1}(\boldsymbol{r}_7)\,\phi_{3a_1}(\boldsymbol{r}_8)\,\phi_{1b_1}(\boldsymbol{r}_9)\,\phi_{1b_1}(\boldsymbol{r}_{10}) \tag{12-96}$$

[where $\boldsymbol{r}_i$ denotes the spatial coordinates of electron i] is given by

$$(A_1)^2 \otimes (A_1)^2 \otimes (B_2)^2 \otimes (A_1)^2 \otimes (B_1)^2 = A_1. \tag{12-97}$$

The symmetry of a product of molecular orbitals is is built up from the MO symmetries and the occupation numbers (0, 1, or 2; a molecular orbital cannot occur more than twice in the Slater determinant as mentioned above) in a way similar to that in which we build up the symmetries of complete vibrational wavefunctions [see, for example, Eq. (12-66)]. MO products corresponding to excited electronic state wavefunctions are obtained by promoting one or more of the electrons out of these MO's into MO's of higher energy. For example, the MO product for the excited $\tilde{A}$ state of water is obtained by promoting an electron out of the ($1b_1$) nonbonding orbital and into the ($3sa_1$) orbital [largely an atomic 3s(O) orbital] to give the configuration

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1(3sa_1)^1 \tag{12-98}$$

which has symmetry B_1.

The occupied molecular orbitals in the lowest electronic state of a molecule cannot always be determined from simple MO arguments such as those just presented. In general, the molecular orbitals obtained in an SCF calculation are LCAO's as given by Eq. (9-69). The SCF calculation yields as result the expansion coefficients of Eq. (9-69), $c_{\mu k}$ [$\mu = 1, 2, 3, \ldots, N_b$; $k = 1, 2, 3, \ldots, N_b$]. The basis functions $\chi_\mu(\boldsymbol{r})$ in this equation can be symmetry classified in the MS group using the techniques outlined above, and from their symmetries, taken together with the known $c_{\mu k}$ values, we can determine the symmetries of the MO's $\phi_k(\boldsymbol{r})$. The MO's will necessarily transform according to irreducible representations of the MS group. The symmetries of MO products, such as that given in Eq. (12-89), can be determined as indicated by Eq. (12-97). We can now classify the orbital part of the Slater determinant in the MS group. However, to classify the complete determinant we must also be able to determine the irreducible representations generated by the electron spin functions. Methods for doing this are discussed in the following two sections.

12.5.2 Hund's case (b) basis functions

It often happens, as for example in the ground electronic states of the CH and NH_2 molecules, that the magnetic coupling of the electron spin to the electron and nuclear orbital motions is small. In these circumstances it is appropriate to use electron spin basis wavefunctions that are quantized along space fixed axes in the same manner that nuclear spin functions were used in Chapter 8. Such a situation is termed *Hund's case* (b) and basis functions in which the electron spin functions are quantized along space fixed axes are termed Hund's case (b) functions. Sometimes spin-orbit coupling is strong so that the electron spin is "tied" to the molecule fixed axis system (for low values of the rotational quantum numbers at least). In these circumstances the wavefunctions are better represented using electron spin functions that are quantized along molecule fixed axes;[4] this is *Hund's case* (a) and a Hund's case (a) basis. We must be able to classify each type of basis set function in the MS group. In Eq. (9-68) we constructed a Slater determinant, and such determinants serve as basis functions for expressing the total electronic wavefunctions $\Phi_{\text{elec}}^{(e,S,m_S)}$, in terms of the one-electron spin functions $\alpha(\sigma)$ and $\beta(\sigma)$, which are quantized along the space-fixed axes (ξ, η, ζ). Consequently, the wavefunctions $\Phi_{\text{elec}}^{(e,S,m_S)}$ are also quantized along these space fixed axes [the quantum number m_S defines the projection of the total electron spin on the ζ axis], and they are Hund's case (b) basis functions. The functions $\alpha(\sigma)$ and $\beta(\sigma)$ are unaffected either by any permutation of identical nuclei or by the inversion operation E^*, so that they are totally symmetric in the MS group. Hence, when spin-orbit coupling is small, so that a Hund's case (b) basis set is appropriate, the symmetry species of the electronic wavefunctions $\Phi_{\text{elec}}^{(e,S,m_S)}$ can be determined without considering the spin functions. The effect of including electron spin in the wavefunction is merely to add a multiplicity label $2S+1$ as a superscript to the species of the electronic wavefunction. For example, for the states discussed for the water molecule we have

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[4] In a Hund's case (a) basis $\hat{T}_N$ [see Eq. (10-150)] involves $\hat{L}_\alpha + \hat{S}_\alpha$ and $\hat{L}_\beta + \hat{S}_\beta$ rather than $\hat{L}_\alpha$ and $\hat{L}_\beta$, respectively.

$$(1\text{a}_1)^2(2\text{a}_1)^2(1\text{b}_2)^2(3\text{a}_1)^2(1\text{b}_1)^2 \quad {}^1A_1 \tag{12-99}$$

and

$$(1\text{a}_1)^2(2\text{a}_1)^2(1\text{b}_2)^2(3\text{a}_1)^2(1\text{b}_1)^1(3\text{sa}_1)^1 \quad {}^1B_1 \quad \text{and} \quad {}^3B_1. \tag{12-100}$$

For singlet states the quantum numbers J, k, and m associated with the solution of the rotational wave equation describe the rovibronic angular momentum of the molecule, its projections along the molecule fixed z axis, and its projection along the space fixed ζ axis. For nonsinglet states in case (b) N and m are used, rather than J and m, since by convention J is then reserved for angular momentum *including* electron spin, and the quantum number specifying the projection of $\boldsymbol{J}$ on the ζ axis is called m_J.

12.5.3 Hund's case (a) basis functions

The operator

$$\hat{s}_{iz} = \lambda_{z\xi}\hat{s}_{i\xi} + \lambda_{z\eta}\hat{s}_{i\eta} + \lambda_{z\zeta}\hat{s}_{i\zeta} \tag{12-101}$$

represents the component along the molecule fixed z axis of the spin angular momentum of electron i. In Eq. (12-101) $(\hat{s}_{i\xi}, \hat{s}_{i\eta}, \hat{s}_{i\zeta})$ are the space fixed components of the spin angular momentum of electron i, and the λ_{zA} are the direction cosines from Eq. (10-5). We obtain electron spin functions quantized along the molecule fixed axes by diagonalizing the matrix representation of $\hat{s}_{iz}$ in the basis $\alpha(\sigma_i)$ and $\beta(\sigma_i)$. The resulting 2×2 matrix has the eigenvalues $-1/2$ and $1/2$, but the eigenfunctions [the new, "molecule fixed" spin functions] depend on the Euler angles because $\hat{s}_{iz}$ depends on these angles through the direction cosines. We now construct Slater determinants in terms of molecule fixed spin functions. For the *ab initio* determination of Φ_{elec} the new choice of spin functions produces no discernible change of the theory outlined in Chapter 9; the reason is that in an *ab initio* calculation, the nuclei are fixed in space, and the Euler angles are thus held constant. However, when we classify the electronic wavefunctions in the MS group we must take into account that not only the products of molecular orbitals entering into the Slater determinants, but also the products of spin functions are now affected by any rotation of the molecule fixed (x, y, z) axes caused by the MS group operations. We can use the fact that if we take the electronic (CI) wavefunction from Eq. (9-83) and insert in this expression the Slater determinant from Eq. (9-68) expanded as $n!$ terms, we obtain the CI wavefunction as a superposition of very many terms, each term being the product of n molecular orbitals multiplied by the product of n spin functions. We have already seen that all the products of n molecular orbitals occurring in the wavefunction will have the same symmetry in the MS group, and the same is true for all the products of n spin functions. Furthermore, the products of spin functions will be such that the total electronic wavefunction is an eigenfunction of $\hat{\boldsymbol{S}}^2$ with eigenvalue $S(S+1)\hbar^2$, exactly as for Hund's case (b) functions. The spin function products will transform according to the irreducible representation $D^{(S)}$ in the group $\boldsymbol{K}$(mol) defined in Chapter 4. To determine the species of the products of electron spin functions in the MS group we use the correlation table[5] of $\boldsymbol{K}$(mol) to the MS group (see Table B-2). For integral values of S this presents no problems. When S is half-integral (i.e., for a molecule with an odd number of electrons) the classification of the spin functions in $\boldsymbol{K}$(mol) and in the MS group presents problems, which we will discuss in Chapter 18. Here, we will complete the general argument and apply it to an example in which the molecule has an even number of electrons.

When Hund's case (a) electron spin functions are used the quantum numbers J, p, and m_J associated with the solution of the rotational equation describe, respectively, the angular momentum of the molecule including electron spin, its projection along the molecule fixed z axis, and its projection along the space fixed ζ axis direction. We consider an example of a molecule with an even number of electrons and show how the symmetry classifications in the Hund's case (a) and (b) limits are made.

We consider a $\boldsymbol{C}_{3v}(\mathrm{M})$ pyramidal XY_3Z molecule, such as CH_3F, in an electronic state of symmetry ${}^3A_2$ and in a totally symmetric, A_1, vibrational state. The species of the rovibronic-electron spin wavefunctions Φ_{rves} is given as $\Gamma_{\mathrm{rves}} = \Gamma_{\mathrm{rv}} \otimes \Gamma_{\mathrm{es}}$, where Γ_{rv} is obtained by multiplying the species of the rotational and vibrational wavefunctions, and Γ_{es} is obtained by multiplying the species of the products of molecular orbital functions and electron spin wavefunctions, respectively, entering into the Slater determinant.

In the Hund's case (b) limit for the CH_3F example the rotational species Γ_{rot} are obtained from Table 12-5, with the replacement of J by N, and these are given on the left in Fig. 12-15. The vibrational species is A_1 and the electronic orbital species [i.e., the species of the products of molecular orbitals entering into the Slater determinant] is A_2 so that the rovibronic species Γ_{rve} are obtained by multiplying Γ_{rot} by A_2. The rovibronic species are given down the center of Fig. 12-15. The triplet electron spin functions are each of symmetry A_1 in case (b) so that the rovibronic-electron spin species Γ_{rves} are as given on the right in Fig. 12-15, and we have $J = N+1, N, N-1$ for a triplet state

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[5] This involves using the equivalent rotations of the MS group and reducing $\boldsymbol{K}$(mol) onto the equivalent rotation group.

(except for $N = 0$ when $J = 1$ only).

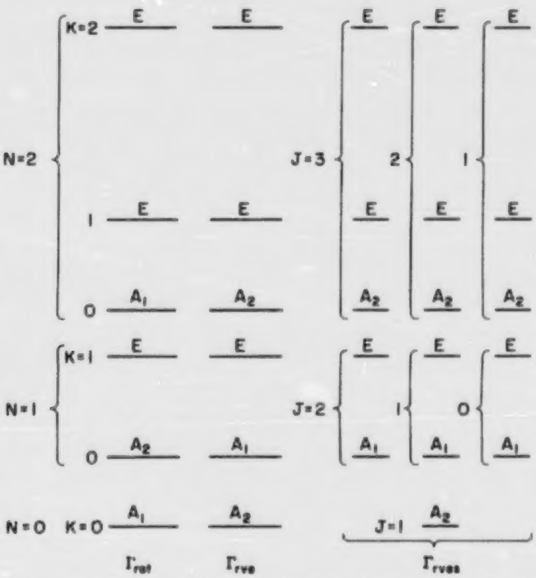

Fig. 12-15. The symmetry labels Γ_{rves} for the rovibronic-electron spin energy levels of the CH_3F molecule in a $^3A_2$ vibronic state using Hund's case (b) electron spin functions and the group $C_{3v}(M)$.

In a Hund's case (a) basis for the CH_3F molecule the electron spin species is obtained first from the reduction of $D^{(1)}$ of $\boldsymbol{K}$(mol) onto $C_{3v}(M)$, and this gives $\Gamma_{\mathrm{espin}} = A_2 \oplus E$. Multiplying by the electronic orbital species A_2 we obtain the electronic spin-orbit species Γ_{eso} as $A_1 \oplus E$ and these two spin-orbit states are split apart by spin-orbit coupling as indicated on the left in Fig. 12-16; in Hund's case (a) this splitting is much larger than the rotational energy level spacings. Multiplying the species Γ_{eso} by the vibrational species A_1 and then by the rotational species Γ_{rot} (obtained from Table 12-5 with the replacement of K by $P = |p|$) we obtain the Γ_{rves} species as given on the right in Fig. 12-16.

As we see by comparing the right hand sides of Figs. 12-15 and 12-16 the case (a) and case (b) rovibronic-electron spin energy level patterns are quite different. In the case (b) limit (Fig. 12-15) the rovibronic-electron spin energy level pattern is like that of a singlet state but every energy level (except that with $N = 0$) is a triplet; a small spin-orbit interaction would make these triplets resolvable. In the case (a) limit the energy level pattern is that of two distinct electronic states (one of which is degenerate). Regardless of the extent of the spin-orbit interaction the rovibronic-electron spin Hamiltonian commutes with the MS group and with $\boldsymbol{K}$(mol) so the symmetry labels J and Γ_{rves} remain valid. Thus we can correlate the case (a) and case (b) rovibronic-electron spin energy levels, maintaining J and Γ_{rves}. The reader can test that this can be

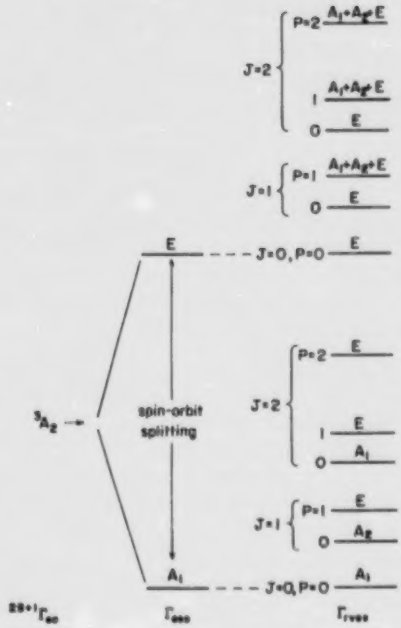
J=2
P=2
A_1+A_2+E
1
A_1+A_2+E
0
E
J=1
P=1
A_1+A_2+E
0
E
E
J=0, P=0
E
J=2
P=2
E
1
E
0
A_1
J=1
P=1
E
0
A_2
$^3A_2$
spin-orbit splitting
A_1
J=0, P=0
A_1
$^{2S+1}\Gamma_{ve}$
Γ_{ves}
Γ_{rves}

Fig. 12-16. The symmetry labels $\Gamma_{\rm rves}$ for the rovibronic-electron spin energy levels of the CH_3F molecule in a $^3A_2$ electronic state (and an A_1 vibrational state) using Hund's case (a) electron spin functions and the group C_{3v}(M).

done and, for example, for $J = 1$ we have the case (a) and case (b) symmetries as follows:

$$\Gamma_{\rm rves}({\rm case(b)}) = A_2 \oplus A_1 \oplus E \oplus A_2 \oplus E \oplus E = A_1 \oplus 2A_2 \oplus 3E \qquad (12\text{-}102)$$

and

$$\Gamma_{\rm rves}({\rm case\ (a)}) = A_2 \oplus E \oplus E \oplus (A_1 \oplus A_2 \oplus E) = A_1 \oplus 2A_2 \oplus 3E. \qquad (12\text{-}103)$$

12.6 NEAR SYMMETRY GROUPS

The rigid rotor Hamiltonian commutes with the elements of the molecular rotation group $\boldsymbol{D}_2$ (the ***four-group*** sometimes called $\boldsymbol{V}$ for *Vierergruppe*) for an asymmetric top molecule, $\boldsymbol{D}_\infty$ for a symmetric top molecule, and $\boldsymbol{K}$(mol) for a spherical top molecule. The vibrational Hamiltonian and electronic Hamiltonian commute with the molecular point group of the molecule. These are all near symmetry groups whose elements do not commute with the full Hamiltonian. Some discussion of these groups, and of the concept of near symmetry, has been given in Chapters 4 and 7, but a more detailed discussion is warranted.

12.6.1 The molecular rotation group

The molecular rotation group of a molecule consists of all Euler angle transformations that leave the rigid rotor Hamiltonian of the molecule invariant, and we can picture each operation of the group as being a bodily rotation of the molecule about an axis that has a definite orientation within the molecule fixed axis system. Each element of the molecular rotation group of a molecule changes the Euler angles but does not transform the vibronic or spin coordinates. The terms in the complete Hamiltonian in which the rotational coordinates are coupled to the vibronic or spin coordinates [such as the Coriolis coupling term Eq. (11-1c) or the term H_{nsr} in Table 7-1] will not necessarily commute with the elements of the molecular rotation group, and they can therefore break this symmetry. However, these effects are sometimes small (particularly in the isolated ground vibronic states usually studied by microwave spectroscopy) and in these circumstances the molecular rotation group provides useful near symmetry labels on the molecular energy levels.

For a spherical top molecule the rigid rotor Hamiltonian is [see Eq. (11-22)] in cm^{-1}

$$\hat{H}_{\text{sph}} = \hbar^{-2} B_e \hat{\boldsymbol{J}}^2. \tag{12-104}$$

This Hamiltonian is invariant to the Euler angle transformation caused by rotation of the molecule about any axis that has a definite orientation within the molecule fixed axis system. Thus the molecular rotation group of a spherical top molecule is $\boldsymbol{K}$(mol); this group provides the label J (or N for non-singlet electronic states) for the levels, and each J level has a $(2J + 1)$-fold k-degeneracy. This degeneracy, and the symmetry in $\boldsymbol{K}$(mol), is removed by interactions such as caused by centrifugal distortion and Coriolis coupling effects.

For a symmetric top molecule the rigid rotor Hamiltonian is [see Eqs. (11-10) and (11-20)] in cm^{-1}

$$\hat{H}_{\text{symm}} = \hbar^{-2}[X_e \hat{\boldsymbol{J}}^2 + (Z_e - X_e)\hat{J}_z^{\,2}], \tag{12-105}$$

where we use the letters X and Z for the rotational constants ($X = B$ and $Z = A$ or C). This Hamiltonian is invariant to the Euler angle transformations caused by any rotation about the molecule fixed z axis and by any twofold rotation about an axis perpendicular to the z axis. It is left as an exercise for the reader to show that the operations R_z^{β} and R_α^{π} (see Table 12-1) commute with $\hat{\boldsymbol{J}}^2$ and $\hat{J}_z^{\,2}$ [see Eqs. (10-84)-(10-86)] and hence with $\hat{H}_{\text{symm}}$. The molecular rotation group of a symmetric top molecule is thus the group $\boldsymbol{D}_\infty$. This group is a subgroup of the group $\boldsymbol{K}$(mol) and the character table is given in Table 12-15. We can classify the symmetric top functions $|J, k, m\rangle$

Table 12-15

The character table of $\boldsymbol{D}_\infty$ and the species of symmetric top functions $|J, \pm K, m\rangle$ in the group

		E	$2R_z^\varepsilon$	$\cdots$	∞R_α^π	Symmetry species as function of K[a]	Symmetry of J_α
Σ^+	:	1	1	$\cdots$	1	0 (J even)	
Σ^-	:	1	1	$\cdots$	-1	0 (J odd)	J_z
Π	:	2	$2\cos\varepsilon$	$\cdots$	0	1	(J_x, J_y)
Δ	:	2	$2\cos 2\varepsilon$	$\cdots$	0	2	
Φ	:	2	$2\cos 3\varepsilon$	$\cdots$	0	3	
$\vdots$		$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\vdots$	

[a] P in Hund's case (a). In nonsinglet states J becomes N.

(or $|N, \boldsymbol{k}, m\rangle$ in nonsinglet states). and the J_α, in $\boldsymbol{D}_\infty$, by using the results in Table 12-1, and Eqs. (12-46) and (12-47); the results of this classification are included in Table 12-15. We see that the distinctions made by classifying the states in $\boldsymbol{D}_\infty$ parallel the distinctions made by using the unsigned quantum number K [or P in Hund's case (a)]. Rotation-vibration levels of different $\boldsymbol{D}_\infty$ species [i.e., of different K (or P) value] can be mixed by, for example, Coriolis coupling terms in the Hamiltonian, and these effects spoil the symmetry of the complete Hamiltonian in $\boldsymbol{D}_\infty$. The symmetry in $\boldsymbol{D}_\infty$, i.e., the quantum number K (or P), deteriorates in usefulness the more vibrationally excited the molecule becomes. This is because the density of vibrational states increases rapidly with vibrational excitation and there is, therefore, more opportunity for rotation-vibration interactions to be significant. This is discussed further in Chapter 13.

Table 12-16

The character table of the group $\boldsymbol{D}_2$ and the species of the asymmetric top functions $|J_{K_a K_c}\rangle$ in the group

		E	R_a^π	R_b^π	R_c^π	$K_a K_c$	Symmetry of J_α
A	:	1	1	1	1	ee	
B_a	:	1	1	-1	-1	eo	J_a
B_b	:	1	-1	1	-1	oo	J_b
B_c	:	1	-1	-1	1	oe	J_c

For an asymmetric top molecule the rigid rotor Hamiltonian (in cm^{-1}) is [see Eq. (11-53)]

$$\hat{H}_{\text{asym}} = \hbar^{-2}(A_e\hat{J}_a{}^2 + B_e\hat{J}_b{}^2 + C_e\hat{J}_c{}^2). \tag{12-106}$$

This Hamiltonian is invariant to the Euler angle transformations caused by a twofold rotation about the a, b, or c axis. The molecular rotation group is hence the group $\boldsymbol{D}_2 = \{E, R_a{}^\pi, R_b{}^\pi, R_c{}^\pi\}$, which is a subgroup of $\boldsymbol{D}_\infty$, and the character table of the $\boldsymbol{D}_2$ molecular rotation group is given in Table 12-16. We can classify the asymmetric rotor wavefunctions in this group by following the procedure used in obtaining Table 12-8, and the results are also included in Table 12-16. For molecules for which the $J_{K_aK_c}$ states ee, oe, eo, and oo transform as four different irreducible representations of the molecular symmetry group we achieve no new distinctions by using the molecular rotation group. However, for molecules for which this is not true, such as trans C(HF)CHF (see Table 12-11) or completely unsymmetrical molecules like CHIFCl, we do obtain extra energy level distinctions that are of great use (particularly for the levels of the vibrational ground state for which the symmetry breaking effects are usually negligible). The factorization of the rigid rotor Hamiltonian into four blocks (see Problem 11-2) follows from the symmetry of the states in the group $\boldsymbol{D}_2$.

The correlation of the species of $\boldsymbol{K}$(mol) to $\boldsymbol{D}_\infty$ and to $\boldsymbol{D}_2$ is given in Table B-1 for $J \leq 3$.

12.6.2 The molecular point group

For any molecule the point group symmetry of the equilibrium nuclear arrangement is easily determined (see Chapter 4). In using the point group to transform molecular wavefunctions the elements of the group are interpreted as being rotations and reflections of the vibronic variables (vibrational displacements and electronic coordinates) in the molecule fixed axis system [see Section 5-5 and Fig. 5-7 in Wilson, Decius, and Cross (1955), and Section 4.5 here]. The molecular point group is a symmetry group of the vibronic Hamiltonian since all interparticle distances are maintained by its elements. The Euler angles, angular momentum components $\hat{J}_\alpha$ and nuclear spin coordinates are not transformed by the elements of the molecular point group. The molecular point group is not used for labeling rovibronic states (rotational levels), but rather for labeling vibrational and electronic states and for studying vibronic interactions. It is a true symmetry group of the vibronic (and electronic) Hamiltonian.

It is important to appreciate exactly how the molecular coordinates transform under the elements of the molecular point group, and to appreciate how the elements are related to the elements of the molecular symmetry group. Some of this ground has already been covered in Section 4.5. We will again use the water molecule as an example.

Locating the molecule fixed (x, y, z) axes on a water molecule as shown in Fig. 10-2 on page 210 (the xz plane is the molecular plane and the x axis is the twofold symmetry axis) the elements of the molecular point group C_{2v} are $\{E, C_{2x}, \sigma_{xz}, \sigma_{xy}\}$ and the character table of this group is as given in Table 12-17. To determine the symmetry of the normal coordinates in this group we first determine the transformation properties of the Cartesian displacement coordinates. The results of doing this are given in Table 12-18. As an example in Fig. 12-17 the effect of C_{2x} on the Δx coordinates is shown, and we see that

$$C_{2x}(\Delta x_1, \Delta x_2, \Delta x_3) = (\Delta x_1', \Delta x_2', \Delta x_3') = (\Delta x_2, \Delta x_1, \Delta x_3). \qquad (12\text{-}107)$$

Table 12-17

The character table of the C_{2v} point group

		E	C_{2x}	σ_{xz}	σ_{xy}
A_1	:	1	1	1	1
A_2	:	1	1	-1	-1
B_1	:	1	-1	-1	1
B_2	:	1	-1	1	-1

Table 12-18

The transformation properties of the Cartesian displacement coordinates of H_2O in the C_{2v} group given in Table 12-17[a]

	E	C_{2x}	σ_{xz}	σ_{xy}	E	C_{2x}	σ_{xz}	σ_{xy}	
	Δx_1	Δx_2	Δx_1	Δx_2	T_x	T_x	T_x	T_x	$: A_1$
	Δx_2	Δx_1	Δx_2	Δx_1	T_y	$-T_y$	$-T_y$	T_y	$: B_1$
	Δx_3	Δx_3	Δx_3	Δx_3	T_z	$-T_z$	T_z	$-T_z$	$: B_2$
	Δy_1	$-\Delta y_2$	$-\Delta y_1$	Δy_2	R_x	R_x	$-R_x$	$-R_x$	$: A_2$
	Δy_2	$-\Delta y_1$	$-\Delta y_2$	Δy_1	R_y	$-R_y$	R_y	$-R_y$	$: B_2$
	Δy_3	$-\Delta y_3$	$-\Delta y_3$	Δy_3	R_z	$-R_z$	$-R_z$	R_z	$: B_1$
	Δz_1	$-\Delta z_2$	Δz_1	$-\Delta z_2$					
	Δz_2	$-\Delta z_1$	Δz_2	$-\Delta z_1$					
	Δz_3	$-\Delta z_3$	Δz_3	$-\Delta z_3$					
χ_{Car}:	9	-1	3	1					

[a] The protons are numbered 1 and 2 and the oxygen nucleus 3. The (x, y, z) axes are defined in Fig. 10-2.

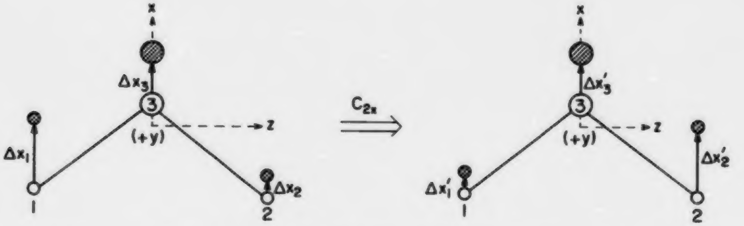

Fig. 12-17. The effect of the molecular point group operation C_{2x} on the x displacement coordinates of the nuclei in H_2O.

The vibrational displacements are rotated about the x axis by C_{2x} but the molecule fixed axes are unaffected. The transformation properties of the translational and rotational combinations of the Cartesian displacement coordinates [see Eq. (12-15)] are also given in Table 12-18, and we deduce the species of the normal coordinates in $\boldsymbol{C}_{2\mathrm{v}}$ to be

$$\Gamma(Q_1, Q_2, Q_3) = 2A_1 \oplus B_2. \tag{12-108}$$

The symmetry of the lower molecular orbitals can be determined from those of the minimal basis set of atomic orbitals 1s(O), 2s(O), $2p_x$(O), $2p_y$(O), $2p_z$(O), 1s(H_1), and 1s(H_2). The transformation properties of these orbitals in the $\boldsymbol{C}_{2\mathrm{v}}$ group are given in Table 12-19. In Fig. 12-18 the effect of C_{2x} on the $2p_z$(O) orbital is shown. Using the LCAO approximation we deduce that the lowest bonding and nonbonding symmetry adapted molecular orbitals of H_2O in the $\boldsymbol{C}_{2\mathrm{v}}$ group, can be written qualitatively as

$$\begin{array}{lll} A_1 & \begin{cases} (1a_1) : \\ (2a_1) : \\ (3a_1) : \end{cases} & \begin{array}{l} 1s(\mathrm{O}), \\ 2s(\mathrm{O}) + [1s(\mathrm{H}_2) + 1s(\mathrm{H}_1)], \\ 2p_x(\mathrm{O}) + [1s(\mathrm{H}_2) + 1s(\mathrm{H}_1)]; \end{array} \\ B_1 & \;\;(1b_1) : & 2p_y(\mathrm{O}); \\ B_2 & \;\;(1b_2) : & 2p_z(\mathrm{O}) + [1s(\mathrm{H}_2) - 1s(\mathrm{H}_1)]. \end{array} \tag{12-109}$$

Comparison of Tables 12-18 and 12-19 with the results given in Table 12-2 and Eq. (12-91), and of Figs. 12-17 and 12-18 with Figs. 12-5 and 12-14, shows that the point group operations C_{2x}, σ_{xz}, and σ_{xy} have the same effect on the vibronic variables in H_2O as the MS group operations (12), E^*, and $(12)^*$, respectively. By studying the point groups of all rigid nonlinear molecules we find that there is a general rule, as already stated in Section 4.5, that:

For a rigid nonlinear molecule the molecular point group and the molecular symmetry group are isomorphic, and each element in the molecular point group has the same effect on the vibronic variables as its partner in the molecular symmetry group.

Since the molecular point group and the molecular symmetry group are isomorphic for rigid nonlinear molecules, we choose (as already stated in Chapter 5) to use common character tables and irreducible representation labels for them and this is done in Appendix ***A***. The results of a classification of vibronic states is then the same using either group.

Table 12-19

The transformation properties of the atomic orbitals in the $\boldsymbol{C}_{2\mathrm{v}}$ group for H_2O

E	C_{2x}	σ_{xz}	σ_{xy}	
1s(O)	1s(O)	1s(O)	1s(O)	: A_1
2s(O)	2s(O)	2s(O)	2s(O)	: A_1
$2p_x(O)$	$2p_x(O)$	$2p_x(O)$	$2p_x(O)$	: A_1
$2p_y(O)$	$-2p_y(O)$	$-2p_y(O)$	$2p_y(O)$	: B_1
$2p_z(O)$	$-2p_z(O)$	$2p_z(O)$	$-2p_z(O)$	: B_2
$1s(H_1)$ $1s(H_2)$	$1s(H_2)$ $1s(H_1)$	$1s(H_1)$ $1s(H_2)$	$1s(H_2)$ $1s(H_1)$	: $A_1 \oplus B_2$

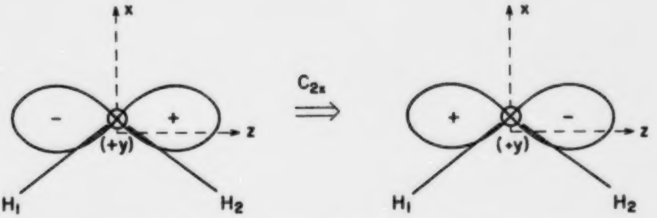

Fig. 12-18. The effect of the molecular point group operation C_{2x} on the $2p_z(O)$ orbital in H_2O.

APPENDIX 12-1: THE TRANSFORMATION PROPERTIES OF THE EULER ANGLES USING EQUATIONS

The water molecule

The transformation of the Euler angles caused by (12) in the water molecule can be derived by using Eqs. (10-43), (10-45), (10-46), (10-48), and (10-49) together with the result [see Eqs. (1-10) and (1-18)]

$$\begin{aligned}(12)(\xi_1,\eta_1,\zeta_1,\xi_2,\eta_2,\zeta_2,\xi_3,\eta_3,\zeta_3) &= (\xi_1{}',\eta_1{}',\zeta_1{}',\xi_2{}',\eta_2{}',\zeta_2{}',\xi_3{}',\eta_3{}',\zeta_3{}') \\ &= (\xi_2,\eta_2,\zeta_2,\xi_1,\eta_1,\zeta_1,\xi_3,\eta_3,\zeta_3). \end{aligned} \tag{12-110}$$

From Eq. (12-110) we deduce that

$$\begin{aligned}(12)(\xi_2-\xi_1) &= -(\xi_2-\xi_1), \\ (12)(\eta_2-\eta_1) &= -(\eta_2-\eta_1),\end{aligned} \tag{12-111}$$

and

$$(12)(\zeta_2-\zeta_1) = -(\zeta_2-\zeta_1).$$

The $\alpha_i{}^{\mathrm{e}}$ are constants [see Eq. (10-38)] unaffected by any symmetry operation. Hence, from Eqs. (10-43), (10-45), (10-46), (10-48), and (10-49),

$$\begin{aligned}&\cos\theta' = -[(\zeta_2-\zeta_1)/(z_2{}^{\mathrm{e}}-z_1{}^{\mathrm{e}})] = -\cos\theta, \\ &\cos\phi' = -\cos\phi, \quad \sin\phi' = -\sin\phi, \\ &\cos\chi' = \cos\chi, \quad \text{and} \quad \sin\chi' = -\sin\chi.\end{aligned} \tag{12-112}$$

From these equations the result in Eq. (12-1) follows.

For the operation E^* we can write

$$E^*(\xi_i,\eta_i,\zeta_i) = (-\xi_i,-\eta_i,-\zeta_i). \tag{12-113}$$

The result in Eq. (12-2) is obtained by using this equation with the expressions for the Euler angles given in Eqs. (10-43)-(10-49).

The methyl fluoride molecule

For a CH_3F molecule in its equilibrium configuration we let the distances of the fluorine and carbon nuclei from the nuclear center of mass be r_F and r_C respectively, the CH bond length be r_H, and the angle α be as defined in Fig. 12-3a; the (x,y,z) coordinates of the nuclei can be written in terms of these four parameters. Using the direction cosine matrix [see Eqs. (10-5)-(10-7)] we can write the (ξ,η,ζ) coordinates of each nucleus in terms of the (x,y,z) coordinates (i.e., in terms of r_F, r_C, r_H, and α) and the Euler angles, i.e.,

$$\begin{aligned}\xi_i &= \lambda_{x\xi}x_i + \lambda_{y\xi}y_i + \lambda_{z\xi}z_i, \\ \eta_i &= \lambda_{x\eta}x_i + \lambda_{y\eta}y_i + \lambda_{z\eta}z_i, \\ \zeta_i &= \lambda_{x\zeta}x_i + \lambda_{y\zeta}y_i + \lambda_{z\zeta}z_i,\end{aligned} \tag{12-114}$$

where

$$\begin{aligned}&x_1 = r_H\sin\alpha, \quad y_1 = 0, \quad z_1 = z_2 = z_3 = -r_C - r_H\cos\alpha, \\ &x_2 = x_3 = -(1/2)r_H\sin\alpha, \quad y_3 = -y_2 = (\sqrt{3}/2)r_H\sin\alpha, \\ &x_C = y_C = x_F = y_F = 0, \quad z_C = -r_C, \quad z_F = r_F.\end{aligned} \tag{12-115}$$

The effect of the operations (123) and (23)* on the Euler angles can now be determined. By definition

$$(123)(\xi_1, \xi_F, \eta_F, \zeta_F) = (\xi_1{}', \xi_F{}', \eta_F{}', \zeta_F{}') = (\xi_3, \xi_F, \eta_F, \zeta_F) \qquad (12\text{-}116)$$

and we write

$$(123)(\theta, \phi, \chi) = (\theta', \phi', \chi'). \qquad (12\text{-}117)$$

From Eq. (12-116) and Eq. (10-7)

$$\zeta_F{}' = \zeta_F, \qquad (12\text{-}118)$$

i.e.,

$$r_F \cos\theta' = r_F \cos\theta. \qquad (12\text{-}119)$$

Thus

$$\cos\theta' = \cos\theta \qquad (12\text{-}120)$$

and since $0 \leq \theta \leq \pi$ this implies that

$$\theta' = \theta. \qquad (12\text{-}121)$$

Similarly

$$\xi_F{}' = \xi_F \quad \text{and} \quad \eta_F{}' = \eta_F, \qquad (12\text{-}122)$$

so that

$$r_F \sin\theta' \cos\phi' = r_F \sin\theta \cos\phi \qquad (12\text{-}123)$$

and

$$r_F \sin\theta' \sin\phi' = r_F \sin\theta \sin\phi. \qquad (12\text{-}124)$$

Since $\theta' = \theta$ these equations imply

$$\cos\phi' = \cos\phi \quad \text{and} \quad \sin\phi' = \sin\phi \qquad (12\text{-}125)$$

and we deduce the result

$$\phi' = \phi. \qquad (12\text{-}126)$$

We finally determine χ', and to do that we use the equation

$$\xi_1{}' = \xi_3, \qquad (12\text{-}127)$$

i.e.,

$$\begin{aligned}(\cos\theta'\cos\phi'\cos\chi' - \sin\phi'\sin\chi')r_H\sin\alpha - \sin\theta'\cos\phi'(r_C + r_H\cos\alpha)\\ = (\cos\theta\cos\phi\cos\chi - \sin\phi\sin\chi)(-1/2)r_H\sin\alpha\\ - (\cos\theta\cos\phi\sin\chi + \sin\phi\cos\chi)(\sqrt{3}/2)r_H\sin\alpha\\ - \sin\theta\cos\phi(r_C + r_H\cos\alpha). \qquad (12\text{-}128)\end{aligned}$$

Since $\phi' = \phi, \theta' = \theta$, and Eq. (12-128) must be true for all θ and ϕ it follows that

$$\sin\chi' = (\sqrt{3}/2)\cos\chi + (-1/2)\sin\chi \qquad (12\text{-}103a)$$

and

$$\cos\chi' = (-1/2)\cos\chi - (\sqrt{3}/2)\sin\chi \qquad (12\text{-}103b)$$

from which we deduce that

$$\chi' = (\chi + 2\pi/3). \qquad (12\text{-}130)$$

The effect of the operation (23)* can be similarly determined from the equations

$$(23)^*(\xi_1, \xi_F, \eta_F, \zeta_F) = (\xi_1', \xi_F', \eta_F', \zeta_F') = (-\xi_1, -\xi_F, -\eta_F, -\zeta_F) \qquad (12\text{-}131)$$

and

$$(23)^*(\theta, \phi, \chi) = (\theta', \phi', \chi'). \qquad (12\text{-}132)$$

From $\xi_F' = -\xi_F, \eta_F' = -\eta_F$, and $\zeta_F' = -\zeta_F$ we deduce that

$$\sin\theta'\cos\phi' = -\sin\theta\cos\phi, \qquad (12\text{-}133)$$

$$\sin\theta'\sin\phi' = -\sin\theta\sin\phi, \qquad (12\text{-}134)$$

and

$$\cos\theta' = -\cos\theta, \qquad (12\text{-}135)$$

respectively. From $\xi_1' = -\xi_1$ we deduce that

$$\begin{aligned}(\cos\theta'\cos\phi'\cos\chi' - \sin\phi'\sin\chi')r_H\sin\alpha - \sin\theta'\cos\phi'(r_C + r_H\cos\alpha)\\ = -(\cos\theta\cos\phi\cos\chi - \sin\phi\sin\chi)r_H\sin\alpha + \sin\theta\cos\phi(r_C + r_H\cos\alpha).\\ (12\text{-}136)\end{aligned}$$

These four equations lead to the solution

$$(\theta', \phi', \chi') = (\pi - \theta, \phi + \pi, \pi - \chi). \qquad (12\text{-}137)$$

APPENDIX 12-2: THE TRANSFORMATION PROPERTIES OF R_α AND T_α

To determine the normal coordinate representation we have determined the representation generated by the $3N$ Cartesian displacement coordinates and subtracted the representation generated by the translational and rotational coordinates T_λ and R_λ, where $\lambda = x, y$, or z [see Eqs. (12-6)-(12-20)]. We therefore need to know the representation generated by the T_λ and the R_λ. In this subsection we show that for asymmetric and symmetric top molecules the transformation properties of R_λ, T_λ, and $\hat{J}_\lambda$ (as well as of the direction cosine matrix elements and vibrational and electronic angular momentum components, $\hat{p}_\lambda$ and $\hat{L}_\lambda$) under the effect of an element from the MS group follow once the equivalent rotation of the MS group element has been determined. For spherical top molecules the symmetry species of these factors is best determined by reduction of their species in the group $\boldsymbol{K}$(mol).

From the results in Table 12-1 the transformation properties of $\hat{J}_x, \hat{J}_y$, and $\hat{J}_z$ under the effect of each element of an MS group follow once the equivalent rotations ($R_z{}^\beta$ or $R_\alpha{}^\pi$) of the elements have been determined. Similarly since the direction cosine matrix elements only involve the Euler angles [see Eq. (10-7)] their transformation properties in the MS group follow from the results in Table 12-1 once the equivalent rotations of the elements have been determined. It turns out that the transformation properties of $(\lambda_{x\tau}, \lambda_{y\tau}, \lambda_{z\tau})$ are the same as those of $(\hat{J}_x, \hat{J}_y, \hat{J}_z)$ regardless of whether $\tau = \xi, \eta$, or ζ. This result follows by application of the discussion that leads to Eq. (6-125), since we can write

$$\hat{J}_\tau = \lambda_{x\tau}\hat{J}_x + \lambda_{y\tau}\hat{J}_y + \lambda_{z\tau}\hat{J}_z, \tag{12-138}$$

and $\hat{J}_\tau$ must be totally symmetric in the MS group, as we now show. $\hat{J}_\tau$ is given by

$$\hat{J}_\tau = \sum_{i,\mu,\nu} \varepsilon_{\tau\mu\nu}\mu_i\hat{P}_{\nu_i}, \tag{12-139}$$

where $\tau, \mu, \nu = \xi, \eta$, or ζ, $\hat{P}_{\nu_i} = -i\hbar\partial/\partial\nu_i$, and $\varepsilon_{\tau\mu\nu}$ is defined in Eq. (10-91). A permutation operation simply interchanges terms $(\mu_i\hat{P}_{\nu_i})$ in the sum over i and the sum, i.e., $\hat{J}_\tau$, is unaffected. The inversion E^* changes the sign of all μ_i and $\hat{P}_{\nu_i}$ so that $\hat{J}_\tau$ is invariant. As a result $\hat{J}_\tau$ is invariant to all elements of the MS group and is totally symmetric. Also following from Eq. (6-125) is the fact that the vibrational angular momenta $\hat{p}_\lambda$ and electronic angular momenta $\hat{L}_\lambda$ transform in the same way as $\hat{J}_\lambda$ (where $\lambda = x, y$, or z) since the terms $\mu^e_{\lambda\lambda}\hat{p}_\lambda\hat{J}_\lambda$ and $\mu^e_{\lambda\lambda}\hat{L}_\lambda\hat{J}_\lambda$ occur in the molecular Hamiltonian and must, therefore, be totally symmetric in the MS group. The representations generated by the three $\hat{J}_\lambda$ for all the MS groups have been determined from the results in Table 12-1 and are given in each of the character tables in Appendix $\boldsymbol{A}$.

The transformation properties of the translational and rotational coordinates T_λ and R_λ can be determined from the equivalent rotations as follows. Suppose

P is a permutation element of the MS group of an asymmetric top or symmetric top molecule. We write this element here as $P[R_\alpha{}^b]$ where $R_\alpha{}^b$ is the equivalent rotation of P (it is either $R_z{}^\beta$ or $R_\alpha{}^\pi$ in the notation of Table 12-1). Suppose that the operation $P[R_\alpha{}^b]$ has the effect of replacing nucleus j by nucleus i [i.e., it contains the permutation $(\cdots ji \cdots)$], then we can write

$$P[R_\alpha{}^b]\lambda_i = \lambda_i' = x_j f_{\lambda x}(R_\alpha{}^b) + y_j f_{\lambda y}(R_\alpha{}^b) + z_j f_{\lambda z}(R_\alpha{}^b), \tag{12-140}$$

where $\lambda = x, y,$ or z, and $f_{\lambda\mu}(R_\alpha{}^b)$ is a function of the angle α or β that defines $R_\alpha{}^b$ (see Table 12-1). For the operation $R_z{}^\beta$ we have

$$\begin{aligned} P[R_z{}^\beta]x_i &= x_j \cos\beta + y_j \sin\beta, \\ P[R_z{}^\beta]y_i &= y_j \cos\beta - x_j \sin\beta, \\ P[R_z{}^\beta]z_i &= z_j, \end{aligned} \tag{12-141}$$

so that

$$\begin{aligned} &f_{xx}(R_z{}^\beta) = f_{yy}(R_z{}^\beta) = \cos\beta, \\ &f_{xy}(R_z{}^\beta) = -f_{yx}(R_z{}^\beta) = \sin\beta, \\ &f_{xz}(R_z{}^\beta) = f_{yz}(R_z{}^\beta) = f_{zx}(R_z{}^\beta) = f_{zy}(R_z{}^\beta) = 0, \\ &f_{zz}(R_z{}^\beta) = 1. \end{aligned} \tag{12-142}$$

For example, in the BF$_3$ molecule (see Fig. 12-6) the operation (123) has the equivalent rotation $R_z^{2\pi/3}$ and we have

$$(123)[R_z^{2\pi/3}]x_3 = x_3' = x_2 \cos(2\pi/3) + y_2 \sin(2\pi/3). \tag{12-143}$$

For the operation $R_\alpha{}^\pi$ we determine that in general

$$\begin{aligned} &f_{xx}(R_\alpha{}^\pi) = -f_{yy}(R_\alpha{}^\pi) = \cos 2\alpha, \\ &f_{xy}(R_\alpha{}^\pi) = f_{yx}(R_\alpha{}^\pi) = \sin 2\alpha, \\ &f_{xz}(R_\alpha{}^\pi) = f_{yz}(R_\alpha{}^\pi) = f_{zx}(R_\alpha{}^\pi) = f_{zy}(R_\alpha^\pi) = 0, \\ &f_{zz}(R_\alpha{}^\pi) = -1. \end{aligned} \tag{12-144}$$

Notice that the $f_{\lambda\mu}(R_\alpha{}^b)$ are the $\lambda\mu$ elements of the three-dimensional representation matrix of the operation $R_\alpha{}^b$ generated by $\hat{J}_x, \hat{J}_y$, and $\hat{J}_z$. For a permutation-inversion element P^* (where P replaces j by i) we similarly write

$$P^*[R_\alpha{}^b]\lambda_i = x_j f^*_{\lambda x}(R_\alpha{}^b) + y_j f^*_{\lambda y}(R_\alpha{}^b) + z_j f^*_{\lambda z}(R_\alpha{}^b), \tag{12-145}$$

and since a permutation-inversion operation changes the signs of all the coordinates we must have

$$f^*_{\lambda\mu}(R_\alpha{}^b) = -f_{\lambda\mu}(R_\alpha{}^b). \tag{12-146}$$

We are now in a position to determine the general effect of the MS group elements $P[R_\alpha{}^b]$ and $P^*[R_\alpha{}^b]$ on the coordinates T_λ and R_λ.

Table 12-20

The transformation properties of the translational coordinates T_x, T_y, and $T_z{}^a$ under the effect of permutations (P) and permutation-inversions (P^*) of an MS group^b

	$P[R_z{}^\beta]$	$P[R_\alpha{}^\pi]$
T_x :	$T_x \cos\beta + T_y \sin\beta$	$T_x \cos 2\alpha + T_y \sin 2\alpha$
T_y :	$-T_x \sin\beta + T_y \cos\beta$	$T_x \sin 2\alpha - T_y \cos 2\alpha$
T_z :	T_z	$-T_z$
	$P^*[R_z{}^\beta]$	$P^*[R_\alpha{}^\pi]$
T_x :	$-T_x \cos\beta - T_y \sin\beta$	$-T_x \cos 2\alpha - T_y \sin 2\alpha$
T_y :	$T_x \sin\beta - T_y \cos\beta$	$-T_x \sin 2\alpha + T_y \cos 2\alpha$
T_z :	$-T_z$	T_z

[a] See Eq. (10-111).

[b] The results are given as a function of the equivalent rotation of each element (see Table 12-1 for the definition of the equivalent rotations).

First we look at the translational coordinates T_λ, and from Eq. (10-111) we have

$$T_\lambda = M_{\mathrm{N}}^{-1/2} \sum_i m_i \Delta\lambda_i, \tag{12-147}$$

and, therefore,

$$P[R_a{}^b]T_\lambda = M_{\mathrm{N}}^{-1/2} \sum_i m_i \Delta\lambda_i' \tag{12-148}$$

$$= M_{\mathrm{N}}^{-1/2} \sum_j m_j \left(\sum_\mu f_{\lambda\mu}(R_a{}^b) \Delta\mu_j \right). \tag{12-149}$$

Equation (12-149) follows from Eq. (12-148) since $m_i = m_j$ (P only permutes identical nuclei) and the sum ($\sum_i = \sum_j$) is over all nuclei in the molecule. We can write Eq. (12-149) as

$$P[R_a{}^b]T_\lambda = \sum_\mu f_{\lambda\mu}(R_a{}^b) T_\mu. \tag{12-150}$$

Similarly

$$P^*[R_a{}^b]T_\lambda = \sum_\mu f^*_{\lambda\mu}(R_a{}^b) T_\mu, \tag{12-151}$$

and from Eq. (12-146) we have

$$P^*[R_a{}^b]T_\lambda = -\sum_\mu f_{\lambda\mu}(R_a{}^b)T_\mu. \qquad (12\text{-}152)$$

From Eq. (12-150) we see that T_λ transforms in the same way as $\hat{J}_\lambda$ under a permutation operation of the MS group but, from Eq. (12-152), T_λ transforms with opposite sign to $\hat{J}_\lambda$ under a permutation-inversion operation. The transformation properties of T_x, T_y, and T_z are given in Table 12-20 under the effect of MS group operations P and P^* as a function of the equivalent rotation of the operations. Using this table the representation of any MS group (of an asymmetric or symmetric top molecule) that is generated by the T_λ can be determined; these species are indicated in the character tables in Appendix ***A***.

To appreciate how the rotational coordinates R_x, R_y, and R_z transform we look in detail at the transformation properties of R_x [see Eq. (10-112)]; R_x is given by

$$R_x = (\mu_{xx}^{\mathrm{e}})^{1/2}\sum_i m_i(y_i{}^{\mathrm{e}}\Delta z_i - z_i{}^{\mathrm{e}}\Delta y_i). \qquad (12\text{-}153)$$

Using $m_i = m_j, \sum_i = \sum_j$, and the relationship between $(y_i{}^{\mathrm{e}}, z_i{}^{\mathrm{e}})$ and $(y_j{}^{\mathrm{e}}, z_j{}^{\mathrm{e}})$ we have

$$\begin{aligned}P[R_z{}^\beta]R_x &= (\mu_{xx}^{\mathrm{e}})^{1/2}\sum_i m_j[(-\sin\beta x_j{}^{\mathrm{e}} + \cos\beta y_j{}^{\mathrm{e}})\Delta z_j \\ &\qquad - z_j{}^{\mathrm{e}}(-\sin\beta\Delta x_j + \cos\beta\Delta y_j)] \\ &= \cos\beta(\mu_{xx}^{\mathrm{e}})^{1/2}\sum_j m_j(y_j{}^{\mathrm{e}}\Delta z_j - z_j{}^{\mathrm{e}}\Delta y_j) \\ &\qquad + \sin\beta(\mu_{xx}^{\mathrm{e}})^{1/2}\sum_j m_j(z_j{}^{\mathrm{e}}\Delta x_j - x_j{}^{\mathrm{e}}\Delta z_j) \\ &= R_x\cos\beta + (\mu_{xx}^{\mathrm{e}}/\mu_{yy}^{\mathrm{e}})^{1/2}R_y\sin\beta. \qquad (12\text{-}154)\end{aligned}$$

For a symmetric top molecule $\mu_{xx}^{\mathrm{e}} = \mu_{yy}^{\mathrm{e}}$ and for an asymmetric top molecule we can only have $\beta = 0$ or π when $\sin\beta = 0$; thus we can effectively write

$$P[R_z{}^\beta]R_x = R_x\cos\beta + R_y\sin\beta \qquad (12\text{-}155)$$

and R_x transforms in the same way as $\hat{J}_x$ under $P[R_z{}^\beta]$. Since R_x involves the products $y_i{}^{\mathrm{e}}\Delta z_i$ and $z_i{}^{\mathrm{e}}\Delta y_i$ the permutation-inversion $P^*[R_z{}^\beta]$ has the same effect as $P[R_z{}^\beta]$ since the sign change from Eq. (12-146) cancels out. Thus R_x transforms as $\hat{J}_x$ under $P[R_z{}^\beta]$ and $P^*[R_z{}^\beta]$. In a similar manner it is possible to show that R_x, R_y, and R_z transform in the same way as $\hat{J}_x, \hat{J}_y$, and $\hat{J}_z$, respectively, under all the elements of the MS group.

13

Energy Levels and Interactions

The interactions that can occur between molecular energy levels are discussed and it is shown how true symmetry labels can be used to determine that some interaction terms vanish and that some levels cannot interact. Near quantum numbers and near symmetry labels can be used to identify the strong interactions. There is much material here; this is the longest chapter of the book. We discuss rotation-vibration, vibronic and rovibronic interactions, as well as the contact transformed rotation-vibration Hamiltonian appropriate for interpreting spectra, and the variational calculation of rotation-vibration energies. We also discuss the Renner and Jahn-Teller effects, the calculation of energy levels in Rydberg states, the effects of electron and nuclear spin, and ortho-para conversion.

13.1 INTRODUCTION

13.1.1 Separable basis functions

The internal Hamiltonian of a molecule $\hat{H}_{\rm int}$ [see Eqs. (7-28) and (7-29), and Table 7-1] is totally symmetric in the MS group and in the group $\boldsymbol{K}$(spatial). In order to determine the eigenvalues and eigenfunctions of $\hat{H}_{\rm int}$, we make the Born-Oppenheimer approximation, we neglect electronic fine structure and nuclear hyperfine structure, we consider the molecular rotation to be independent of the vibration [in that we describe the rotation as that of a rigid molecule], and we take the Born-Oppenheimer potential energy function $V_{\rm N}$ for the one electronic state under study to be harmonic [in that we only retain the leading term $\frac{1}{2}\sum_r \lambda_r {Q_r}^2$ in Eq. (10-143)]. By making all these approximations we obtain a simplified internal Hamiltonian $\hat{H}^0_{\rm int}$ whose eigenfunctions are the approximate (zero order) wavefunctions

$$\Phi^0_{\rm int} = \Phi_{\rm nspin}\Phi_{\rm rot}\Phi_{\rm vib}\Phi_{\rm elec}^{(e,S,m_S)} \qquad (13\text{-}1)$$

where the electronic wavefunction $\Phi_{\mathrm{elec}}^{(e,S,m_S)}$ is defined on page 195. The zero order wavefunction Φ_{int}^{0} is *separable* in that it can be written as a product of wavefunctions, each being a function of only the coordinates appropriate to a particular set of degrees of freedom. We can classify each of these wavefunctions in the MS group and in the group $\boldsymbol{K}$(spatial).

We determine the eigenvalues and eigenfunctions of the true internal Hamiltonian H_{int} by diagonalizing its matrix representation in the basis of the separable functions Φ_{int}^{0}. That is, we employ the technique described in Eqs. (6-144)-(6-162) with the separable functions Φ_{int}^{0} playing the role of the basis functions Ψ_{n}^{0} in these equations, and we obtain the true eigenfunctions of H_{int}, Φ_{int}, as linear combinations of the basis functions Φ_{int}^{0},

$$\Phi_{\mathrm{int}}^{(j)} = \sum_{n} C_{jn}\Phi_{\mathrm{int},n}^{0} \tag{13-2}$$

[see Eq. (6-148)], where the index j numbers the eigenfunctions of H_{int}, the index n numbers the separable basis functions, and the C_{jn} are the expansion coefficients calculated as eigenvector coefficients in the diagonalization of the Hamiltonian matrix. Since H_{int} is totally symmetric in the MS group and in $\boldsymbol{K}$(spatial), each $\Phi_{\mathrm{int}}^{(j)}$ function will be a linear combination of $\Phi_{\mathrm{int},n}^{0}$ having the same symmetry in each of these two groups. Thus each final (exact) wavefunction $\Phi_{\mathrm{int}}^{(j)}$ bears the same true symmetry labels as the approximate wavefunctions $\Phi_{\mathrm{int},n}^{0}$ of which it is composed (see Chapter 6). As a result of this we can use the symmetry of the approximate wavefunctions to determine these final labels and to determine which zero order molecular energy levels can interact with each other. This procedure is only useful for labeling the true energy levels if there is a largely unambiguous semi-quantitative match between the true energy levels and the zero order energy levels that go along with the zero order Φ_{int}^{0} of Eq. (13-1). This enables the true energy levels to be correctly assigned. For nonrigid molecules (including weakly bound cluster molecules), or molecules subject to the Renner or Jahn-Teller effect, or molecules in Rydberg states, a different zero order starting point is appropriate.

The MS group label Γ_{int} obtained by classifying the approximate wavefunctions Φ_{int}^{0}, is not the only MS group symmetry label that is useful when studying molecular interactions. The MS group labels on the basis set wavefunctions Φ_{nspin}, Φ_{rot}, Φ_{vib}, and $\Phi_{\mathrm{elec}}^{(e,S,m_S)}$ are Γ_{nspin}, Γ_{rot}, Γ_{vib}, and Γ_{elec}, respectively. These labels, or combinations of them, are called basis symmetry labels and they are useful for studying various interactions between Φ_{int}^{0} states: Configuration interaction can only occur between states having the same Γ_{elec} label, anharmonicity can only couple states having the same Γ_{vib} label, rotation-vibration interactions can only occur between states having the same $\Gamma_{\mathrm{rv}}(=\Gamma_{\mathrm{rot}}\otimes\Gamma_{\mathrm{vib}})$ label, vibronic interactions can only occur between states having the same $\Gamma_{\mathrm{ve}}(=\Gamma_{\mathrm{vib}}\otimes\Gamma_{\mathrm{elec}})$ label, rovibronic interactions can only occur between states having the same $\Gamma_{\mathrm{rve}}(=\Gamma_{\mathrm{rot}}\otimes\Gamma_{\mathrm{vib}}\otimes\Gamma_{\mathrm{elec}})$ label, and so on. These rules result from the fact that each interaction term involves only some of the coordinates in the molecule and can, therefore, only affect that part of the zero order wavefunction that involves these coordinates. Invariably only certain interactions are important in a particular case, and only certain basis symmetry labels are needed in the discussion of the interactions occurring. Usually Hund's case (b) is appropriate and we can often neglect electronic fine structure and nuclear hyperfine structure (i.e., the effects of the interactions of the electronic and nuclear spins with the other degrees of freedom). The basis symmetry labels we would use in this case to determine which rovibronic states can interact would be Γ_{rve}, from the MS group, and N (called J for singlet states) from the group $\boldsymbol{K}$(spatial). These are the symmetry labels that are appropriate for studying the most common interactions that occur between molecular energy levels.

13.1.2 Near quantum numbers

Obviously, if the zero order Hamiltonian H^0_{int} is a good approximation to the true Hamiltonian H_{int}, then the eigenfunctions of H_{int}, $\Phi^{(j)}_{\mathrm{int}}$, will be very similar to the eigenfunctions of H^0_{int}, $\Phi^0_{\mathrm{int},j}$. That is, when $\Phi^{(j)}_{\mathrm{int}}$ is normalized we have in Eq. (13-2) $|C_{jj}| \approx 1$ and $|C_{jn}| \ll 1$ for $n \neq j$. The two functions $\Phi^{(j)}_{\mathrm{int}}$ and $\Phi^0_{\mathrm{int},j}$ are sufficiently similar that we can use the quantum numbers and symmetry labels of $\Phi^0_{\mathrm{int},j}$ to label the true molecular eigenstate $\Phi^{(j)}_{\mathrm{int}}$. The quantum numbers defining $\Phi^0_{\mathrm{int},j}$ will be ***near quantum numbers*** and its symmetry labels are ***near symmetry labels*** as discussed in Chapter 7.

To illustrate the idea of near quantum numbers, we consider the rotational Hamiltonian of an asymmetric top [Eq. (11-55)]. In diagonalizing the Hamiltonian we use a $|J, k_a, m\rangle$ basis set where $\hat{J}_a{}^2(= \hat{J}_z{}^2)$ has eigenvalues $K_a{}^2\hbar^2$. If $(B-C)$ were zero then Eq. (11-55) would reduce to the rotational Hamiltonian of a symmetric top and the functions $|J, k_a, m\rangle$ would be its eigenfunctions. As far as the rotational Hamiltonian of a prolate symmetric top is concerned the quantum number K_a is a ***good quantum number*** in that states having different values of K_a are not mixed by any terms in that Hamiltonian. The rotational Hamiltonian of a symmetric top has the symmetry of the $\boldsymbol{D}_\infty$ molecular rotation group. For an asymmetric top if $B-C$ were small (compared to A, B, or C) then the $\boldsymbol{D}_\infty$ symmetry breaking effects of the term $(B-C)[(\hat{J}^+_{\mathrm{m}})^2 + (\hat{J}^-_{\mathrm{m}})^2]/4$ would be slight and the asymmetric top states would largely consist of one K_a state with a small admixture of states having different K_a values. For example, for the ground state of the SO_2 molecule the rotational constants are approximately

$$A = 2.0\ \mathrm{cm}^{-1}, \quad B = 0.34\ \mathrm{cm}^{-1}, \quad \text{and} \quad C = 0.29\ \mathrm{cm}^{-1}.$$

Thus $B-C = 0.05\ \mathrm{cm}^{-1}$ which is small compared to the rotational constants. From Eqs. (11-78)-(11-80) we deduce from these values of A, B, and C that the two $J = 2$ states of type E^+ can be written in terms of $|J, k_a, m\rangle$ functions as follows :

$$\Phi^- = 0.99992|2,0,m\rangle - 0.01284(|2,2,m\rangle + |2,-2,m\rangle)/\sqrt{2}, \tag{13-3}$$

$$\Phi^+ = 0.01284|2,0,m\rangle + 0.99992(|2,2,m\rangle + |2,-2,m\rangle)/\sqrt{2}. \tag{13-4}$$

Clearly Φ^- is very closely a $K_a = 0$ state and Φ^+ is very closely a $K_a = 2$ state. The quantum number K_a is a useful ***near quantum number*** for determining which are the important perturbations of the states of an asymmetric top molecule, such as SO_2, that is a near prolate top. For a near oblate top, i.e., for $A_e \approx B_e$, K_c is a useful near quantum number. For an asymmetric top molecule having a large degree of asymmetry [i.e., $\kappa \approx 0$, see Eq. (11-84)] neither K_a nor K_c is a useful near quantum number in this regard. However, each does provide a convenient unambiguous label for the energy levels, and asymmetric top energy levels are labeled $J_{K_aK_c}$. The labels K_a and K_c also allow the symmetry in $\boldsymbol{D}_2$ or in the MS group to be simply determined by consideration of their evenness or oddness.

The eigenfunctions of a one-dimensional harmonic oscillator Hamiltonian are labeled by the vibrational quantum number v. For a harmonic oscillator v is a good quantum number. For the low vibrational states of an anharmonic oscillator, v is a useful near quantum number in that each state consists mainly of one v state. For a two-dimensional harmonic oscillator l is an additional quantum number that is spoiled by Coriolis coupling and centrifugal distortion, and for a three-dimensional harmonic oscillator n is also used. The vibrational states of polyatomic molecules are labeled using the near quantum numbers v, l, and n as appropriate, e.g., in methane the vibrational states are labeled by the values of $v_1, v_2, v_3, v_4, l_2, l_3, l_4, n_3$, and n_4. Such labels are useful near quantum number labels as long as severe mixing between states having different labels does not take place. For example, in the CO_2 molecule the (v_1, v_2, v_3) states (0,2,0) and (1,0,0) for $l_2 = 0$ are heavily mixed so that for these states the quantum numbers v_1 and v_2 are not useful near quantum numbers. The relationship between the vibrational quantum numbers, the degeneracies of the levels, and an appropriate near symmetry group has been discussed many times [see, for example, Baker (1956) and Hwa and Nuyts (1966)].

For the rigid rotor rotational states of a symmetric top molecule the quantum number K is a true quantum number, but it is a near quantum number for the rotation-vibration or rovibronic states. This quantum number is spoiled by centrifugal distortion and Coriolis coupling effects. As a result of the fact that the Hamiltonian of a molecule commutes with the operation of time reversal (which sends every wavefunction into its complex conjugate; see Chapter 7) each eigenstate always involves the sum or difference of the $\boldsymbol{k} = K$ and $\boldsymbol{k} = -K$ wavefunctions. The ***energy levels*** should therefore be labeled using the unsigned quantum number K rather than the signed quantum number $\boldsymbol{k}$. The quantum number J is a near quantum number label for the complete internal states E_{int}

and it is spoiled by, for example, the nuclear spin coupling term $\hat{H}_{\rm nsr}$. However, F is always a good quantum number label for an isolated molecule in free space.

Usually near symmetry labels and near quantum numbers are just called symmetry labels and quantum numbers. In the rest of this chapter we will see that they provide very useful extra restrictions on allowed interactions. While not rigorously true these restrictions do enable us to understand the main interactions in a molecule.

13.1.3 Interaction selection rules

Near symmetry labels and near quantum numbers are generally spoiled by interactions, since the interacting states can have different near symmetry labels or near quantum number labels. However, a level labeled by certain near symmetry labels and near quantum number labels can only be mixed, by a particular interaction, with levels having certain other near symmetry labels and near quantum number labels. As a result there are *selection rules* on the near symmetry labels and near quantum number labels for allowed interactions, and these are very useful.

For a symmetric top molecule in a singlet electronic state the near quantum numbers that label the energy levels are I, J, K, $(\pm l)$, $(v_1, v_2, \ldots, v_s^{l_s}, v_t^{l_t}, \ldots)$ and the occupation numbers $(n_1, n_2, \ldots)$ of the molecular orbitals in the single configuration electronic wavefunction used to describe the state; for nonsinglet states in Hund's case (b) we use N (instead of J) and S. The use of the $(\pm l)$ quantum number label for the levels of a symmetric top molecule in degenerate vibronic states is discussed later in this chapter. For an asymmetric top molecule we use K_a and K_c instead of K, and there are no l_s quantum numbers. For a spherical top molecule we do not use K, and for each three-dimensional harmonic oscillator state we use the quantum numbers v, l, and n (see the end of Section 11.3.2); there is also the quantum number R which we discuss at the end of Section 13.2.3. Each type of interaction mixes states according to definite selection rules for these quantum numbers. Near symmetry labels on the energy levels are obtained by using the molecular point group and the molecular rotation group. The basis symmetry labels $\Gamma_{\rm nspin}$, $\Gamma_{\rm rot}$, $\Gamma_{\rm vib}$, and $\Gamma_{\rm elec}$, discussed previously, are really the same as near symmetry labels on $\Phi_{\rm int}$, and states having different such labels can be mixed. For example, a rotation-vibration interaction (such as Coriolis interaction) mixes states having the same $\Gamma_{\rm rv}$ label but possibly different $\Gamma_{\rm rot}$ and $\Gamma_{\rm vib}$ labels; a level in H_2O having $\Gamma_{\rm rot} = A_1$, and $\Gamma_{\rm vib} = B_2$, can be mixed by a rotation-vibration interaction with a level having $\Gamma_{\rm rot} = B_2$ and $\Gamma_{\rm vib} = A_1$, since both have $\Gamma_{\rm rv} = B_2$. The MS group basis symmetry labels $\Gamma_{\rm vib}, \Gamma_{\rm elec}$, and $\Gamma_{\rm ve}$ are the same as the near symmetry labels from the molecular point group for a rigid nonlinear molecule.

In the discussion above, we have assumed the detailed form of the internal Hamiltonian $\hat{H}_{\rm int}$ to be known. Hence it would seem that in obtaining the eigenvalues and eigenfunctions of $\hat{H}_{\rm int}$, the only use we can make of symmetry, in the form of the MS group and the group $\boldsymbol{K}$(spatial), is to classify the basis states Φ^0_{int} in these groups, thus determining which pairs of basis functions give rise to nonvanishing off-diagonal matrix elements of $\hat{H}_{\mathrm{int}}$. When $\hat{H}_{\mathrm{int}}$ is known we should then be able to calculate these nonvanishing matrix elements and diagonalize the corresponding matrix blocks. However, when we use the theory outlined in Eqs. (13-1) and (13-2) to construct models for interpreting an experimental spectrum of a particular molecule, we will often find that we know only the general form of the molecular Hamiltonian given by Eqs. (11-1a)-(11-1d) together with Eqs. (10-150)-(10-154). In these equations, the Hamiltonian is written as a general expansion in the normal coordinates, and all the expansion coefficients in these series are assumed to be nonvanishing. The fact that $\hat{H}_{\mathrm{int}}$ is totally symmetric in the MS group can be used to show that for a particular molecule, very many of these expansion coefficients will vanish. In practical applications of Eqs. (13-1) and (13-2) to the interpretation of molecular spectra, we will typically start by using symmetry to decide which pairs of basis functions can interact [i.e., can produce nonvanishing off-diagonal matrix elements of $\hat{H}_{\mathrm{int}}$] as discussed above. However, before we can use this knowledge to calculate the matrix representation of $\hat{H}_{\mathrm{int}}$ we must determine the detailed form of the interaction terms in it which produce the nonvanishing matrix elements. That is, we must identify the totally symmetric terms in the general expression for $\hat{H}_{\mathrm{int}}$. We often wish to determine the terms in the Hamiltonian responsible for a particular interaction between basis states having (zero order) energies that are close (i.e., *"in resonance"*). We have to investigate the totally symmetric terms in the Hamiltonian and find those that couple particular, selected basis functions, i.e., those that produce nonvanishing matrix elements with particular selection rules on the near quantum numbers such as K, v and l.

Each interaction term in the Hamiltonian couples certain degrees of freedom that are separate in zero order. Terms that spoil the separation of electronic and vibrational motion give rise to ***vibronic interactions***, terms that couple the electronic degrees of freedom with both the vibrational and the rotational motion cause ***rovibronic interactions***, terms that couple the vibrational and rotational motions give rise to ***rotation-vibration interactions***, terms that couple the electron spin and electron orbital degrees of freedom give rise to ***spin-orbit interactions***, and terms that couple the nuclear spins to the other degrees of freedom can give rise to so-called ***ortho-para mixing***. Vibronic and rovibronic interactions are manifestations of the breakdown of the Born-Oppenheimer approximation and we give a special discussion of the important examples of this that are provided by the Renner effect, the Jahn-Teller effect and the calculation of the energy levels of Rydberg states. The interactions described here are discussed using the true symmetry labels as well as the basis symmetry labels and the near symmetry labels. The variational calculation of rotation-vibration energies is given a special discussion.

13.2 ROTATION-VIBRATION INTERACTIONS

We discuss perturbations occurring within an electronic state, caused by terms in the rotation-vibration Hamiltonian. These perturbations are caused by anharmonicity, centrifugal distortion, and Coriolis coupling effects and the corresponding terms in the Hamiltonian are written as [see Eqs. (11-1b)-(11-1d) and Eqs. (10-151) and (10-154)]

$$V_{\mathrm{anh}} = \frac{1}{6}\sum_{r,s,t}\Phi_{rst}Q_rQ_sQ_t + \frac{1}{24}\sum_{r,s,t,u}\Phi_{rstu}Q_rQ_sQ_tQ_u + \cdots , \tag{13-5}$$

$$\begin{aligned} T_{\mathrm{cent}} = &-\frac{1}{2}\sum_{\alpha,\beta,r}\mu^{\mathrm{e}}_{\alpha\alpha}a_r^{\alpha\beta}\mu^{\mathrm{e}}_{\beta\beta}Q_r\hat{J}_\alpha\hat{J}_\beta \\ &+\frac{3}{8}\sum_{\alpha,\beta,\gamma,r,s}\mu^{\mathrm{e}}_{\alpha\alpha}a_r^{\alpha\gamma}\mu^{\mathrm{e}}_{\gamma\gamma}a_s^{\gamma\beta}\mu^{\mathrm{e}}_{\beta\beta}Q_rQ_s\hat{J}_\alpha\hat{J}_\beta + \cdots , \end{aligned} \tag{13-6}$$

and

$$T_{\mathrm{Cor}} = -\sum_{\alpha,r,s}\mu^{\mathrm{e}}_{\alpha\alpha}\zeta^{\alpha}_{r,s}Q_r\hat{P}_s\hat{J}_\alpha + \cdots . \tag{13-7}$$

In all of the terms in Eqs. (13-5)-(13-7), the total power of momentum operators [$\hat{P}_r$ and $\hat{J}_\alpha$] is even since the total Hamiltonian must be Hermitian and invariant to time reversal [see Chapter 7]. Each of these terms is the product of a *coupling coefficient*, such as Φ_{rst} or $-\mu^{\mathrm{e}}_{\alpha\alpha}\zeta^{\alpha}_{r,s}$ and a *coupling operator*, such as $Q_rQ_sQ_t$ or $Q_r\hat{P}_s\hat{J}_\alpha$. Since each of them must be totally symmetric in the molecular symmetry group of the molecule under consideration (each term is part of the complete rotation-vibration Hamiltonian $\hat{H}_{\mathrm{rv}}$, and $\hat{H}_{\mathrm{rv}}$ is totally symmetric in the MS group), the coupling coefficient must vanish if the coupling operator is not totally symmetric. If the coupling operator is totally symmetric the coupling coefficient could still vanish, but this would be an accident. We can write the following rules, where we use the notation that $\Gamma(x)$ is the symmetry species of x in the MS group:

Φ_{rst} can be nonvanishing only if

$$\Gamma(Q_r)\otimes\Gamma(Q_s)\otimes\Gamma(Q_t)\supset\Gamma^{(s)}, \tag{13-8}$$

Φ_{rstu} can be nonvanishing only if

$$\Gamma(Q_r)\otimes\Gamma(Q_s)\otimes\Gamma(Q_t)\otimes\Gamma(Q_{\mathrm{u}})\supset\Gamma^{(s)}, \tag{13-9}$$

$a_r^{\alpha\beta}$ can be nonvanishing only if

$$\Gamma(Q_r)\otimes\Gamma(\hat{J}_\alpha)\otimes\Gamma(\hat{J}_\beta)\supset\Gamma^{(s)}, \tag{13-10}$$

or, equivalently, only if

$$\Gamma(\hat{J}_\alpha)\otimes\Gamma(\hat{J}_\beta)\supset\Gamma(Q_r)^{*}, \tag{13-11}$$

and $\zeta^{\alpha}_{r,s}$ can be nonvanishing only if

$$\Gamma(Q_r) \otimes \Gamma(\hat{P}_s) \otimes \Gamma(\hat{J}_\alpha) \supset \Gamma^{(s)}, \tag{13-12}$$

or, equivalently, only if

$$\Gamma(Q_r) \otimes \Gamma(Q_s) \supset \Gamma(\hat{J}_\alpha)^*, \tag{13-13}$$

since

$$\Gamma(\hat{P}_s) = \Gamma(Q_s). \tag{13-14}$$

In the above $\Gamma^{(s)}$ is the totally symmetric representation of the MS group. The particular Coriolis coupling parameter $\zeta^{\alpha}_{ta,tb}$, where the normal coordinates (Q_{ta}, Q_{tb}) span a doubly degenerate irreducible representation Γ_t, is nonvanishing if

$$\{\Gamma_t\}^2 \supset \Gamma(\hat{J}_\alpha), \tag{13-15}$$

where $\{\Gamma_t\}^2$ is the antisymmetric product representation [see Eq. (6-120)].

In a rigid rotor harmonic oscillator basis the rotation-vibration perturbation terms mix states according to definite selection rules on the vibrational quantum numbers v_i, l_i (for doubly degenerate vibrations) and n_i (for triply degenerate vibrations), and rotational quantum numbers k, k_a and k_c. For asymmetric top and symmetric top molecules, we discuss these selection rules, and the way that the corresponding perturbations spoil the near quantum numbers v_i, l_i and k should be appreciated. The rotation-vibration species $\Gamma_{\rm rv}$ is maintained in these perturbations. Having derived the selection rules for the interacting states, we also determine the detailed form of the terms in the rotation-vibration Hamiltonian which cause selected perturbations. We need the results for the transformation properties of rotational and translational coordinates derived in Chapter 10. For molecules containing degenerate representations and degenerate normal coordinates it is necessary to choose a convention for the transformation properties of the individual members of each set of degenerate normal coordinates before the equations can be applied [see Eqs. (12-69)–(12-72)]. In Problem 13-3 below such a case is discussed.

13.2.1 Asymmetric top molecules

As an example of an asymmetric top molecule, we consider H_2O in its electronic ground state; the ground electronic state wavefunction [see Eq. (12-95)] is totally symmetric in the MS group $C_{2v}(M)$ [Table A-5]. The water molecule has three normal coordinates with symmetries

$$\begin{aligned} \Gamma(Q_1) = \Gamma(Q_2) &= A_1, \\ \Gamma(Q_3) &= B_2. \end{aligned} \tag{13-16}$$

We diagonalize a matrix representation of the rotation-vibration Hamiltonian in a basis of products $|v_1\rangle|v_2\rangle|v_3\rangle|J, k_a, m\rangle$, where $|v_r\rangle$, $r = 1, 2$, or 3, is a one-dimensional harmonic oscillator function depending on the normal coordinate Q_r, and $|J, k_a, m\rangle$ is a symmetric top function. We use $|J, k_a, m\rangle$ basis functions corresponding to a $\mathrm{I^r}$ convention so that the z axis is chosen along the a axis. It follows from Eq. (12-66) that the vibrational basis function $|v_1\rangle|v_2\rangle|v_3\rangle$ has A_1 symmetry if v_3 is even and B_2 symmetry if v_3 is odd. Further, the symmetry classification of the function $|J, k_a, m\rangle$ is given in Table 12-7. As a result the $|v_1\rangle|v_2\rangle|v_3\rangle|J, k_a, m\rangle$ functions generate the irreducible representations of $C_{2v}(\mathrm{M})$ given in Table 13-1. To summarize the results in Table 13-1: Two basis states of H_2O, $|v_1'\rangle|v_2'\rangle|v_3'\rangle|J, k_a', m\rangle$ and $|v_1\rangle|v_2\rangle|v_3\rangle|J, k_a, m\rangle$, can interact if $\Delta v_3 = v_3' - v_3$ and $\Delta k_a = k_a' - k_a$ are both even, or if Δv_3 and Δk_a are both odd. There are no restrictions on v_1 and v_2. The fact that the rotation-vibration Hamiltonian is totally symmetric in $\boldsymbol{K}$(spatial) means the only pairs of basis states with the same values of J and the same values of m can interact.

It follows from Eqs. (13-8) and (13-9) that in the rotation-vibration Hamiltonian of H_2O, Φ_{rst} and Φ_{rstu} can be nonvanishing only if the index 3 occurs an even number of times in rst and $rstu$, respectively. That is, for a term proportional to $Q_1^{n_1}Q_2^{n_2}Q_3^{n_3}$ to occur in the potential energy function, n_3 must be even. Table A-5 shows that with the $\mathrm{I^r}$ convention $[abc = zxy]$ used here for labeling the molecular axes, J_x has A_2 symmetry, J_y has B_2 symmetry, and J_z has B_1 symmetry. From Eq. (13-11), we derive that $a_r^{\alpha\alpha}$ is nonvanishing for $\alpha = x, y$, or z and $r = 1$ or 2. However all coefficients $a_r^{\alpha\beta}$ with $\alpha \neq \beta$ will vanish except $a_3^{xz} = a_3^{zx}$. Of the $\zeta_{r,s}^{\alpha}$ parameters, only $\zeta_{1,3}^{y} = -\zeta_{3,1}^{y}$ and $\zeta_{2,3}^{y} = -\zeta_{3,2}^{y}$ are nonvanishing.

Table 13-1

Representations of the $C_{2v}(\mathrm{M})$ group for H_2O generated by basis functions $|v_1\rangle|v_2\rangle|v_3\rangle|J, k_a, m\rangle^a$

v_3 even		v_3 odd	
K_a	Γ_{rv}	K_a	Γ_{rv}
0 J even	A_1	0 J even	B_2
J odd	B_1	J odd	A_2
odd	$A_2 \oplus B_2$	odd	$A_1 \oplus B_1$
even	$A_1 \oplus B_1$	even	$A_2 \oplus B_2$

[a] $K_a = |k_a|$.

Table 13-2

Nonvanishing matrix elements of the vibrational and rotational operators

Operator[a]	Nonvanishing matrix elements[b]
Q_r	$\langle v_r + 1 \vert Q_r \vert v_r \rangle$, $\langle v_r - 1 \vert Q_r \vert v_r \rangle$
$\hat{P}_r$	$\langle v_r + 1 \vert \hat{P}_r \vert v_r \rangle$, $\langle v_r - 1 \vert \hat{P}_r \vert v_r \rangle$
$Q_{t\sigma}$, $\sigma = a$ or b	$\langle v_t + 1, l_t + 1 \vert Q_{t\sigma} \vert v_t, l_t \rangle$, $\langle v_t - 1, l_t + 1 \vert Q_{t\sigma} \vert v_t, l_t \rangle$, $\langle v_t + 1, l_t - 1 \vert Q_{t\sigma} \vert v_t, l_t \rangle$, $\langle v_t - 1, l_t - 1 \vert Q_{t\sigma} \vert v_t, l_t \rangle$
$\hat{P}_{t\sigma}$, $\sigma = a$ or b	$\langle v_t + 1, l_t + 1 \vert \hat{P}_{t\sigma} \vert v_t, l_t \rangle$, $\langle v_t - 1, l_t + 1 \vert \hat{P}_{t\sigma} \vert v_t, l_t \rangle$ $\langle v_t + 1, l_t - 1 \vert \hat{P}_{t\sigma} \vert v_t, l_t \rangle$, $\langle v_t - 1, l_t - 1 \vert \hat{P}_{t\sigma} \vert v_t, l_t \rangle$
$Q_t^{\pm} = Q_{ta} \pm iQ_{tb}$	$\langle v_t + 1, l_t \pm 1 \vert Q_t^{\pm} \vert v_t, l_t \rangle$, $\langle v_t - 1, l_t \pm 1 \vert Q_t^{\pm} \vert v_t, l_t \rangle$
$\hat{P}_t^{\pm} = \hat{P}_{ta} \pm i\hat{P}_{tb}$	$\langle v_t + 1, l_t \pm 1 \vert \hat{P}_t^{\pm} \vert v_t, l_t \rangle$, $\langle v_t - 1, l_t \pm 1 \vert \hat{P}_t^{\pm} \vert v_t, l_t \rangle$
$\hat{J}_\alpha$, $\alpha = x$ or y	$\langle J, k + 1, m \vert \hat{J}_\alpha \vert J, k, m \rangle$, $\langle J, k - 1, m \vert \hat{J}_\alpha \vert J, k, m \rangle$
$\hat{J}_z$	$\langle J, k, m \vert \hat{J}_z \vert J, k, m \rangle$
$\hat{J}_{\mathrm{m}}^{\pm} = \hat{J}_x \pm i\hat{J}_y$	$\langle J, k \mp 1, m \vert \hat{J}_{\mathrm{m}}^{\pm} \vert J, k, m \rangle$

The ± and ∓ signs are correlated for each operator involving them.

[a] The normal coordinate Q_r [with conjugate momentum $\hat{P}_r$] transforms according to a nondegenerate irreducible representation of the MS group in question. The normal coordinates (Q_{ta}, Q_{tb}) [with conjugate momenta $(\hat{P}_{ta}, \hat{P}_{tb})$] transform according to a doubly degenerate irreducible representation of the MS group.

[b] The functions $|v_r\rangle$, $|v_t, l_t\rangle$, and $|J, k, m\rangle$ are eigenfunctions for the Hamiltonians of the one-dimensional harmonic oscillator, the two-dimensional harmonic oscillator, and the rigid symmetric rotor, respectively. Expressions for the matrix elements summarized here are given in Tables 11-1, 11-2, and 11-3.

In this example we look at the interactions that can occur between the three vibrational states ν_1, ν_3 and $2\nu_2$ of the water molecule, and discuss the terms in the Hamiltonian that cause them. Figure 13-1 shows a low-resolution experimental spectrum of the atmosphere at ambient conditions, recorded with an absorption path length of approximately 1 m. It is seen that at certain wavenumbers, the water molecules in the atmosphere absorb almost 50% of the incident radiation energy. This absorption is due to transitions in the ν_3 band, which is much stronger than the ν_1 and $2\nu_2$ bands. The upper states of the ν_3 band transitions are perturbed by ν_1 and $2\nu_2$ states [Flaud and Camy-Peyret (1974)] and we study these perturbations here. The three states are associated with the vibrational basis functions $|v_1\rangle|v_2\rangle|v_3\rangle = |1\rangle|0\rangle|0\rangle$ (A_1),

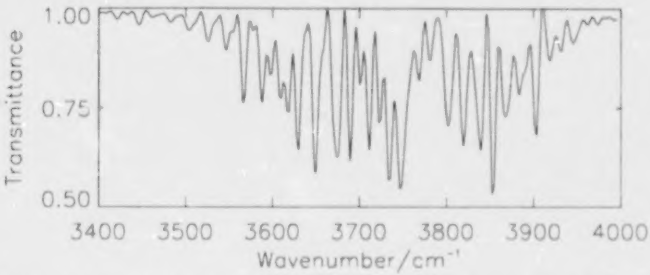

Fig. 13-1. A low-resolution spectrum of the atmosphere at ambient conditions, recorded with an absorption path length of approximately 1 m [Bürger (1998)]. The strong absorption is due to the ν_3 band of H_2O (with band center at 3756 cm^{-1}) which is much stronger than the ν_1 band (with band center at 3657 cm^{-1}) and the $2\nu_2$ band (with band center at 3152 cm^{-1}).

$|0\rangle|0\rangle|1\rangle$ (B_2), and $|0\rangle|2\rangle|0\rangle$ (A_1), respectively, where, for each state, we have given the vibrational symmetry $\Gamma_{\rm vib}$ in parentheses.

The interaction between ν_1 and ν_3: We determine nonvanishing matrix elements $\langle v_1', v_2', v_3'; J, k_a', m|H|v_1, v_2, v_3; J, k_a, m\rangle = \langle 0, 0, 1; J, k_a', m|H|1, 0, 0; J, k_a, m\rangle$. Since $\Delta v_3 = 1$ is odd, then in order for this matrix element not to vanish, Δk_a is also odd [Table 13-1], and the smallest possible value for $|\Delta k_a|$ is 1. We have established that an interaction between ν_1 and ν_3 with $(\Delta v_1, \Delta v_2, \Delta v_3, \Delta k_a) = (-1, 0, 1, \pm 1)$ is allowed by the symmetry in the MS group. We wish to know which of the perturbation terms in Eqs. (13-5)-(13-7) are responsible for this interaction.

Table 13-2 summarizes the nonvanishing matrix elements of the "primitive" operators Q_r, $\hat{P}_r$, $\hat{J}_x$, ..., which enter into the coupling operators of the perturbation terms. From the information given in Table 13-2, we can deduce the nonvanishing matrix elements generated by powers of the primitive operators. Q_r^n will have nonvanishing matrix elements with $\Delta v_r = \pm n, \pm(n-2), \pm(n-4), \ldots, \pm 1$ if n is odd or $\Delta v_r = \pm n, \pm(n-2), \pm(n-4), \ldots, 0$ if n is even [see also Eq. (11-125)]. Similar arguments can be applied to the higher powers of the other operators given in Table 13-2. From the table, we recognize that in order to produce an interaction with $\Delta v_1 = -1$, the coupling operator must contain at least one power of Q_1 or $\hat{P}_1$. If the coupling operator contains more powers of these operators, $Q_1^{n_1}\hat{P}_1^{m_1}$, then $n_1 + m_1$ must be odd. Similarly, in order that $\Delta v_3 = 1$, the coupling operator must contain a product of $Q_3^{n_3}\hat{P}_3^{m_3}$ with $n_3 + m_3$ odd, and in order that $\Delta v_2 = 0$, the coupling operator must contain $Q_2^{n_2}\hat{P}_2^{m_2}$ with $n_2 + m_2$ even. Finally, for Δk_a to be ± 1, then the coupling operator must contain at least one power of $\hat{J}_x$ or $\hat{J}_y$. Generally, it must contain a product $\hat{J}_x{}^{n_x}\hat{J}_y{}^{n_y}$ with $n_x + n_y$ odd. The simplest operator from

Eqs. (13-5)-(13-7) that satisfies these conditions is

$$-\mu^e_{yy}\zeta^y_{1,3}\left(Q_1\hat{P}_3 - Q_3\hat{P}_1\right)\hat{J}_y, \qquad (13\text{-}17)$$

the leading term in the operator T_{Cor} of Eq. (13-7). Other terms that satisfy the conditions are from T_{cent} [Eq. (13-6)]:

$$\frac{3}{8}\left[\mu^e_{xx}a_1^{xx}\mu^e_{xx}a_3^{xz}\mu^e_{zz} + \mu^e_{xx}a_3^{xz}\mu^e_{zz}a_1^{zz}\mu^e_{zz}\right]Q_1Q_3\left(\hat{J}_x\hat{J}_z + \hat{J}_z\hat{J}_x\right), \qquad (13\text{-}18)$$

and from T_{Cor} [Eq. (13-7)]:

$$-\frac{3}{2}\mu^e_{yy}a_1^{yy}\mu^e_{yy}a_2^{yy}\mu^e_{yy}\zeta^y_{2,3}Q_1Q_2\left(Q_2\hat{P}_3 - Q_3\hat{P}_2\right)\hat{J}_y. \qquad (13\text{-}19)$$

We can produce other acceptable coupling operators by multiplying the coupling operators of Eqs. (13-17)-(13-19) by $Q_1^{n_1}Q_2^{n_2}Q_3^{n_3}$, where the integers n_1, n_2, and n_3 are all even. These terms come from the higher expansion terms of Eqs. (13-6)-(13-7). We expect, however, that the expansions in Eqs. (13-6)-(13-7) will converge in the sense that the perturbation terms become less important as the powers of Q_r, $\hat{P}_r$ and $\hat{J}_\alpha$ increase. Thus the terms in Eqs. (13-17)-(13-18) give the most important contributions to the interaction between the ν_1 and ν_3 states. The interaction caused by the Coriolis coupling term in Eq. (13-17) can be termed a *Coriolis-type resonance*. The particular interaction caused by the term in Eq. (13-18) is called a *Birss resonance* [Birss (1976)].

The interaction between ν_1 *and* $2\nu_2$: The terms in V_{anh} [Eq. (13-5)] cannot contribute to the matrix elements coupling ν_1 and ν_3; they contain no rotational operators at all and thus their nonvanishing matrix elements have $\Delta k_a = 0$. They can, however, contribute to the interaction between ν_1 and $2\nu_2$. Since a matrix element connecting ν_1 and $2\nu_2$ has Δv_3 even ($= 0$), Δk_a must also be even [Table 13-1]. The smallest possible value for $|\Delta k_a|$ is 0, and interactions of this type can be caused by the terms in V_{anh}. Since $\Delta v_1 = -1$ and $\Delta v_2 = 2$, an acceptable term must contain an odd power of Q_1 and an even power (≥ 2) of Q_2. The simplest term that satisfies these conditions is

$$\frac{1}{2}\Phi_{122}Q_1Q_2^2 \qquad (13\text{-}20)$$

from Eq. (13-5). Again, we can construct other acceptable coupling operators by multiplying the coupling operator $Q_1Q_2^2$ in Eq. (13-20) by $Q_1^{n_1}Q_2^{n_2}Q_3^{n_3}$, where the integers n_1, n_2, and n_3 are all even, but we expect that the term in Eq. (13-20) will give the largest contribution to the coupling matrix elements arising from V_{anh}.

A resonance such as this, in which coupling is caused by terms in the potential energy function, is referred to as an anharmonic resonance. Anharmonic resonances are called cubic, quartic, quintic, ... if they are caused by the cubic, quartic, quintic, ... terms in the expansion of V_{anh} in Eq. (13-5). Cubic anharmonic resonances are also called *Fermi resonances*; this type of resonance was recognized for the first time for the ν_1 and $2\nu_2$ states of CO_2. A *Darling-Dennison resonance* is a particular type of quartic anharmonic resonance involving overtone levels of two normal modes ν_j and ν_k, and it has $\Delta v_j = -\Delta v_k = \pm 2$.

Higher-order terms in T_{cent} [Eq. (13-6)], mainly

$$-\frac{3}{4}\sum_{\alpha=x,y,z} \mu^{\mathrm{e}}_{\alpha\alpha}a_1^{\alpha\alpha}\mu^{\mathrm{e}}_{\alpha\alpha}a_2^{\alpha\alpha}\mu^{\mathrm{e}}_{\alpha\alpha}a_2^{\alpha\alpha}\mu^{\mathrm{e}}_{\alpha\alpha}Q_1Q_2^2\hat{J}_\alpha^2, \qquad (13\text{-}21)$$

can also contribute to the matrix elements connecting ν_1 and $2\nu_2$. For $\alpha = x$ or y, the matrix elements will have $\Delta k_a = 0, \pm 2$ [see Table 13-2], whereas for $\alpha = z$, $\Delta k_a = 0$ only.

The interaction between ν_3 and $2\nu_2$: Here again we have Δv_3 odd, as for the interaction between ν_1 and ν_3, and we must have Δk_a odd. The dominant perturbation terms, causing interactions with $|\Delta k_a| = 1$, come from T_{Cor} and T_{cent} and contain the coupling operators

$$\frac{3}{2}\mu^{\mathrm{e}}_{yy}a_1^{yy}\mu^{\mathrm{e}}_{yy}a_2^{yy}\mu^{\mathrm{e}}_{yy}a_2^{yy}\mu^{\mathrm{e}}_{yy}\zeta^y_{1,3}Q_1Q_2^2\left(Q_1\hat{P}_3 - Q_3\hat{P}_1\right)\hat{J}_y, \qquad (13\text{-}22)$$

$$\mu^{\mathrm{e}}_{yy}a_2^{yy}\mu^{\mathrm{e}}_{yy}\zeta^y_{2,3}Q_2\left(Q_2\hat{P}_3 - Q_3\hat{P}_2\right)\hat{J}_y, \qquad (13\text{-}23)$$

and

$$\begin{aligned} -\frac{1}{4}\big[&\mu^{\mathrm{e}}_{xx}a_2^{xx}\mu^{\mathrm{e}}_{xx}a_2^{xx}\mu^{\mathrm{e}}_{xx}a_3^{xz}\mu^{\mathrm{e}}_{zz} \\ &+ \mu^{\mathrm{e}}_{xx}a_2^{xx}\mu^{\mathrm{e}}_{xx}a_3^{xz}\mu^{\mathrm{e}}_{zz}a_2^{zz}\mu^{\mathrm{e}}_{zz} \\ &+ \mu^{\mathrm{e}}_{xx}a_3^{xz}\mu^{\mathrm{e}}_{zz}a_2^{zz}\mu^{\mathrm{e}}_{zz}a_2^{zz}\mu^{\mathrm{e}}_{zz}\big]Q_2^2Q_3\left(\hat{J}_x\hat{J}_z + \hat{J}_z\hat{J}_x\right). \end{aligned} \qquad (13\text{-}24)$$

Table 13-2 can be used to check that these operators will produce nonvanishing matrix elements with the desired values of $(\Delta v_1, \Delta v_2, \Delta v_3, \Delta k_a)$.

In their simultaneous analysis of experimental spectra of the ν_1, ν_3 and $2\nu_2$ bands of H_2O, Flaud and Camy-Peyret (1974) take into account the resonances caused by the operators in Eqs. (13-18), (13-20), (13-21), and (13-24). They do not consider the Coriolis-type resonances caused by the operators in in Eqs. (13-17), (13-19), (13-22), and (13-23). Initially, one would perhaps expect the neglected operator in Eq. (13-17) to be more important than that in Eq. (13-18), since the former operator involves a lower power of the rotational operators. However, the coupling coefficient in Eq. (13-17) is small due to the small value of $\zeta^y_{1,3}$.

Problem 13-1. Determine the nonvanishing $\Phi, a^{\alpha\beta}$, and ζ^α coefficients for the ground electronic state of the trans diimide molecule (N_2H_2). This molecule is shown in its planar equilibrium configuration in Fig. 13-2 and we assume that there is no torsional tunneling. The MS group of this molecule is $C_{2h}(M)$ [see Table A-8 where the permutation (56) should be omitted].

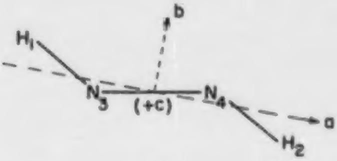

Fig. 13-2. A nuclear labeled diimide molecule in the equilibrium configuration of its ground electronic state. The inertial axes (a, b, c) are also marked $(I_{aa} < I_{bb} < I_{cc})$.

Answer. The six normal coordinates of this molecule have the symmetry species:

$$\begin{aligned} \Gamma(Q_1) = \Gamma(Q_2) = \Gamma(Q_3) &= A_g, \\ \Gamma(Q_4) &= A_u, \\ \Gamma(Q_5) = \Gamma(Q_6) &= B_u. \end{aligned} \tag{13-25}$$

From these results and the rules of Eqs. (13-8) and (13-9) we deduce that the following Φ coefficients do not vanish by symmetry:

$$\Phi_{pqr}, \Phi_{p44}, \Phi_{ptu}, \Phi_{pqrs}, \Phi_{pq44}, \Phi_{pqtu}, \Phi_{44tu}, \Phi_{4444}, \text{ and } \Phi_{tuvw}, \tag{13-26}$$

where p, q, r, and $s = 1, 2$, or 3, and t, u, v, and $w = 5$ or 6. From Eq. (13-11) and the symmetries of $\hat{J}_a, \hat{J}_b, \hat{J}_c$ (given in Table A-8) and of the Q_r, we deduce that the following $a^{\alpha\beta}$ coefficients do not vanish by symmetry

$$a_r^{cc}, a_r^{ab} = a_r^{ba}, a_r^{aa}, \text{ and } a_r^{bb}, \tag{13-27}$$

where $r = 1, 2$, or 3. For the u vibrations of a centrosymmetric molecule all $a_r^{\alpha\beta}$ vanish since the species of the components of $\hat{\boldsymbol{J}}$ are always g (the operation $\hat{O}_i$ that defines the g or u character does not affect the Euler angles). As a result the rotational levels of g and u vibrational states cannot be mixed by the centrifugal distortion perturbation [see Eq. (4-11) and the discussion after it]. From Eq. (13-13) we see that the nonvanishing Coriolis coupling coefficients are

$$\zeta_{p,q}^{c}, \zeta_{5,6}^{c}, \zeta_{4,t}^{a}, \text{ and } \zeta_{4,t}^{b}, \tag{13-28}$$

where $p, q = 1, 2$, or 3 and $t = 5$ or 6. The rotational levels of g and u vibrational states cannot be mixed by the Coriolis coupling perturbation since the $\hat{J}_\alpha$ all have g species, and all $\zeta_{r,s}^{\alpha}$ involving one g and one u vibration must vanish [see Eq. (4-11) and the discussion after it].

Problem 13-2. In the trans diimide molecule N_2H_2 the states $v_4 = 1$ and $v_6 = 1$ are close together in energy. Using the results obtained in the solution to Problem 13-1 determine the direct interactions that can occur between the rotational levels of these states.

Answer. The states $v_4 = 1$ and $v_6 = 1$ have vibrational symmetry $\Gamma_{\text{vib}} = A_u$ and B_u, respectively. Since they have different vibrational symmetries they cannot be mixed by anharmonicity perturbations. The first term in the centrifugal distortion perturbation [see Eq. (13-6)] contains the coupling operator $Q_r\hat{J}_\alpha\hat{J}_\beta$, and hence can couple rotation-vibration states according to the vibrational selection rule $\Delta v_r = \pm 1$. This term cannot give rise to a perturbation between states, such as the $v_4 = 1$ and $v_6 = 1$ states, that differ in two vibrational quantum numbers. The second term in T_{cent} [see Eq. (13-6)] contains the coupling operator $Q_rQ_s\hat{J}_\alpha\hat{J}_\beta$ and this term can couple states that differ in two vibrational quantum numbers. In $C_{2h}(M)$ the combinations $Q_4Q_6\hat{J}_a\hat{J}_c$ and $Q_4Q_6\hat{J}_b\hat{J}_c$ are totally symmetric and we might expect levels of the $v_4 = 1$ and $v_6 = 1$ states to be coupled by such terms. However, the coefficients of $Q_4Q_6\hat{J}_a\hat{J}_c$ and $Q_4Q_6\hat{J}_b\hat{J}_c$ vanish for trans diimide, since they involve the parameters $a_4^{\alpha\beta}$ and $a_6^{\alpha\beta}$ which were shown to be zero in the solution of Problem 13-1 [see Eq. (13-27)]. In the solution to Problem 13-1 we saw that for any centrosymmetric molecule $a_r^{\alpha\beta}$ vanishes if Q_r is of u species, and hence the rotational levels of two vibrational states cannot be connected by T_{cent} if the levels have different levels of excitation of any u vibrations. This contrasts with the fact that the rotational levels for N_2H_2 of the $v_2 = 1$ and $v_3 = 1$ vibrational states (both of A_g symmetry) can be mixed by terms such as $Q_1Q_3J_a{}^2$ in T_{cent} since $a_r^{\alpha\alpha}$ and a_r^{ab} do not vanish for $r = 1$ or 3.

The rotational levels of the $v_4 = 1$ and $v_6 = 1$ states can be mixed by the Coriolis coupling perturbation

$$-\sum_\alpha \mu_{\alpha\alpha}^e \zeta_{4,6}^\alpha (Q_4\hat{P}_6 - Q_6\hat{P}_4)\hat{J}_\alpha. \tag{13-29}$$

In particular $\zeta_{4,6}^a$ and $\zeta_{4,6}^b$ are nonvanishing [see Eq. (13-28)] so that the two nonvanishing coupling terms are (in cm^{-1})

$$V_{\text{Cor}}^{(a)} = -2A\hbar^{-2}\zeta_{4,6}^a(Q_4\hat{P}_6 - Q_6\hat{P}_4)\hat{J}_a \tag{13-30}$$

and

$$V_{\text{Cor}}^{(b)} = -2B\hbar^{-2}\zeta_{4,6}^b(Q_4\hat{P}_6 - Q_6\hat{P}_4)\hat{J}_b. \tag{13-31}$$

These perturbations can only connect levels of the $v_4 = 1$ and $v_6 = 1$ states that have the same J value and Γ_{rv} symmetry. There are two possible Γ_{rv} symmetries for these levels (see Table 12-11): A_u and B_u. The A_u levels are the $J_{K_aK_c}$ levels of the $v_4 = 1$ state having K_c even and the levels of the $v_6 = 1$ state having K_c odd; these levels can be mixed by $V_{\text{Cor}}^{(a)} + V_{\text{Cor}}^{(b)}$. The K_c odd levels in the $v_4 = 1$ state and the K_c even levels of the $v_6 = 1$ state are of B_u symmetry, and they can also be mixed together. Using a I^r prolate rotor basis set (trans diimide is a near prolate rotor) the nonvanishing matrix elements are (from Tables 11-1 and 11-2)

$$\langle v_4 = 1, J, k_a|V_{\text{Cor}}^{(a)}|v_6 = 1, J, k_a\rangle = 2iA\zeta_{4,6}^a[\sqrt{\gamma_6/\gamma_4} + \sqrt{\gamma_4/\gamma_6}]k_a/2 \tag{13-32}$$

and

$$\begin{aligned}&\langle v_4 = 1, J, k_a \pm 1 | V^{(b)}_{\mathrm{Cor}} | v_6 = 1, J, k_a \rangle \\ &\quad = 2iB\zeta^b_{4,6}[\sqrt{\gamma_6/\gamma_4} + \sqrt{\gamma_4/\gamma_6}]\frac{1}{4}\sqrt{J(J+1) - k_a(k_a \pm 1)},\end{aligned} \tag{13-33}$$

where the γ_r parameters are defined in Eq. (11-106). We see that states having high K_a and $K_a \approx J$ will be strongly coupled by $V^{(a)}_{\mathrm{Cor}}$ and weakly coupled by $V^{(b)}_{\mathrm{Cor}}$, whereas those with high J and $K_a \approx 0$ will be strongly coupled by $V^{(b)}_{\mathrm{Cor}}$ and weakly coupled by $V^{(a)}_{\mathrm{Cor}}$.

A spectrum of the ν_4 and ν_6 fundamental bands of N_2H_2 at a resolution of 0.06 cm^{-1} has been analyzed by Hallin, Johns and Trombetti (1981), and at a resolution of 0.005 cm^{-1} by Hegelund, Bürger and Polanz (1994). They determined, among other things, that $\nu_4 = 1288.639\ \mathrm{cm}^{-1}$, $\nu_6 = 1316.413\ \mathrm{cm}^{-1}$, $|\zeta^a_{4,6}| = 0.460$ and $|\zeta^b_{4,6}| = 0.897$. In this analysis higher order terms had to be included in each of the expressions for the matrix elements given in Eqs. (13-32) and (13-33), and it was also necessary to include a matrix element between the ν_4 and ν_6 levels with $\Delta K_a = \pm 2$ in order to achieve a fitting to the spectrum. These are all modeled satisfactorily using the contact transformation procedure discussed in Section 13.2.4.

The Coriolis coupling constants of a molecule satisfy linear and quadratic sum rules called *ζ-sum rules* [see, for example, Teller (1934), Meal and Polo (1956a, 1956b), Watson (1971a), and Section 22.2 of Papousek and Aliev (1982)]. For N_2H_2 the application of these rules gives the relations

$$(\zeta^a_{4,5})^2 + (\zeta^a_{4,6})^2 = 1, \tag{13-34}$$

and

$$(\zeta^b_{4,5})^2 + (\zeta^b_{4,6})^2 = 1. \tag{13-35}$$

N_2H_2 is an example of a centrosymmetric molecule in which one u vibration (ν_4) couples with only two others (ν_5 and ν_6). In this circumstance it can be shown [Kuchitsu, Oka and Morino (1965)] that

$$|\zeta^a_{4,6}| = |\zeta^b_{4,5}| \tag{13-36}$$

and

$$|\zeta^b_{4,6}| = |\zeta^a_{4,5}|. \tag{13-37}$$

Combining these relations with the ζ-sum rules in Eqs. (13-34) and (13-35) we deduce that

$$(\zeta^a_{4,6})^2 + (\zeta^b_{4,6})^2 = 1. \tag{13-38}$$

The experimental value for this sum from Hegelund, Bürger and Polanz (1994) is 1.016.

13.2.2 Symmetric top molecules

For symmetric top molecules we use symmetry, as shown in Section 12.4, to define the "good" quantum numbers g_{rv}, η, and τ, as well as g, g_{ev}, and g_{v}. These quantum numbers are related to the quantum number K, and they obey selection rules for allowed interactions [see Hougen (1962c), Mills (1964a) and Hegelund, Rasmussen, and Brodersen (1973)]; they are very useful when it comes to writing a computer program to calculate rotation-vibration energies.

When we consider matrix elements of the rotation-vibration Hamiltonian $\hat{H}_{\mathrm{rv}}$ between rotation-vibration basis functions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}$ [see Eq. (12-73)] we can use the nonvanishing integral rule to determine the conditions that have to be fulfilled by the quantum numbers g_{rv}, η, and τ. Thus, for

$$\left\langle \Phi_{\mathrm{rv}}^{(V',L',J',k',m')} \middle| \hat{H}_{\mathrm{rv}} \middle| \Phi_{\mathrm{rv}}^{(V'',L'',J'',k'',m'')} \right\rangle \neq 0$$

we must have

$$\Delta g_{\mathrm{rv}} = g'_{\mathrm{rv}} - g''_{\mathrm{rv}} = 0 \tag{13-39}$$

and

$$\Delta \eta = \eta' - \eta'' = 0. \tag{13-40}$$

For Type II basis functions (see Section 12.4) we must also have

$$\Delta \tau = \tau' - \tau'' = 0. \tag{13-41}$$

As usual we consider the CH_3F molecule [MS group $C_{3v}(M)$; see Table A-6] as an example of a symmetric top molecule. The symmetry species of its normal coordinates in the MS group are given by

$$\begin{aligned} \Gamma(Q_1) = \Gamma(Q_2) = \Gamma(Q_3) = A_1, \\ \Gamma(Q_{4a}, Q_{4b}) = \Gamma(Q_{5a}, Q_{5b}) = \Gamma(Q_{6a}, Q_{6b}) = E, \end{aligned} \tag{13-42}$$

so that each vibrational state is characterized by six v quantum numbers $(v_1, v_2, v_3, v_4, v_5, v_6)$ and three l quantum numbers (l_4, l_5, l_6). For this molecule we determine from Eq. (13-39) and Table 12-14 that, within one electronic state, rotation-vibration interactions occur between basis states that satisfy

$$\Delta(l_4 + l_5 + l_6 - k) = 0, \pm 3, \pm 6, \text{ etc.} \tag{13-43}$$

The selection rule for anharmonicity perturbations [i.e., perturbations caused by V_{anh} in Eq. (13-5)] is

$$\Delta g_{\mathrm{v}} = 0, \tag{13-44}$$

and such perturbations have $\Delta k = 0$ and will occur between vibrational states that satisfy

$$\Delta(l_4 + l_5 + l_6) = 0, \pm 3, \pm 6, \text{ etc.} \tag{13-45}$$

Vibronic interactions and rovibronic interactions satisfy the selection rules $\Delta g_{\mathrm{ve}} = 0$ and $\Delta g = 0$, respectively.

Problem 13-3. Determine the nonvanishing $\Phi, a^{\alpha\beta}$, and ζ^{α} coefficients for the CH_3F molecule in its ground electronic state. The CH_3F molecule is labeled in Fig. 13-3 and its MS group is the $C_{3v}(M)$ group given in Table A-6.

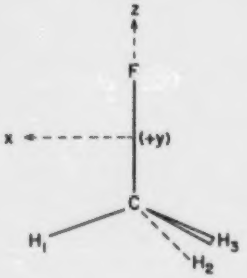

Fig. 13-3. A nuclear labeled methyl fluoride molecule in the equilibrium configuration of its ground electronic state. The (x, y, z) axes are the inertial axes $(I_{zz} < I_{xx} = I_{yy})$.

Answer. The symmetry species of the normal coordinates for CH_3F in $C_{3v}(M)$ are given by Eq. (13-42), and transformation properties of the primitive operators entering into the rotation-vibration Hamiltonian are given in Table 12-4. In the $C_{3v}(M)$ group we have

$$\begin{aligned} A_1 \otimes A_1 &= A_2 \otimes A_2 = A_1, \\ A_1 \otimes E &= A_2 \otimes E = E, \\ E \otimes E &= A_1 \oplus A_2 \oplus E, \\ [E]^2 &= A_1 \oplus E. \end{aligned} \tag{13-46}$$

From Eqs. (13-8) and (13-9), together with the species of the normal coordinates, given in Eq. (13-42), we deduce that the following anharmonic force constants can be nonvanishing:

$$\Phi_{pqr}, \Phi_{rst}, \Phi_{stu}, \Phi_{opqr}, \Phi_{qrst}, \Phi_{rstu}, \text{ and } \Phi_{stuv}, \tag{13-47}$$

where $o, p, q, r = 1, 2$, or 3, and $s, t, u, v = 4, 5$, or 6. For the degenerate vibrations we need to know how the a and b labels should be added, i.e., is Φ_{rst} to be taken as Φ_{rsata}, Φ_{rsatb}, Φ_{rsbta}, or Φ_{rsbtb}? We determine this from the transformation properties of products such as $Q_r Q_{sa} Q_{ta}$ which can be obtained from the results in Table 12-4. We find that the following combination is totally symmetric:

$$(Q_r Q_{sa} Q_{ta} + Q_r Q_{sb} Q_{tb}) = Q_r (Q_s{}^{+} Q_t{}^{-} + Q_s{}^{-} Q_t{}^{+})/2, \tag{13-48}$$

where $Q_s^{\pm}$ and $Q_t^{\pm}$ are related to (Q_{sa}, Q_{sb}) and (Q_{ta}, Q_{tb}) as discussed in Chapter 11 [see Eqs. (11-146)-(11-149) and (11-155)-(11-156)]. Thus

$$\Phi_{rsata} = \Phi_{rsbtb} (= \Phi_{rst}, \text{ say}) \tag{13-49}$$

can be nonvanishing, but

$$\Phi_{rsatb} = \Phi_{rsbta} = 0. \tag{13-50}$$

The potential function, therefore, can contain the terms

$$\Phi_{rst} Q_r (Q_{sa} Q_{ta} + Q_{sb} Q_{tb}) = \Phi_{rst} Q_r (Q_s^+ Q_t^- + Q_s^- Q_t^+)/2. \tag{13-51}$$

The other nonvanishing cubic anharmonicity terms that involves the degenerate normal coordinates are

$$\begin{aligned} &\Phi_{stu}(Q_{sa}Q_{ta}Q_{ua} - Q_{sb}Q_{ta}Q_{ub} - Q_{sb}Q_{tb}Q_{ua} - Q_{sa}Q_{tb}Q_{ub}) \\ &\quad = \Phi_{stu}(Q_s^+ Q_t^+ Q_u^+ + Q_s^- Q_t^- Q_u^-)/2. \end{aligned} \tag{13-52}$$

Quartic anharmonicity terms involving the degenerate normal coordinates that are totally symmetric in $C_{3v}(\mathrm{M})$ and which therefore can be nonvanishing are

$$\begin{aligned} &\Phi_{qrst} Q_q Q_r (Q_s^+ Q_t^- + Q_s^- Q_t^+)/2, \\ &\Phi_{rstu} Q_r (Q_s^+ Q_t^+ Q_u^+ + Q_s^- Q_t^- Q_u^-)/2, \\ &\Phi_{sstu} Q_s^+ Q_s^- (Q_t^+ Q_u^- + Q_t^- Q_u^+)/2, \\ &\Phi'_{sstu} (Q_s^+ Q_s^+ Q_t^- Q_u^- + Q_s^- Q_s^- Q_t^+ Q_u^+)/2. \end{aligned} \tag{13-53}$$

The nonvanishing $a^{\alpha\beta}$ coefficients are determined from Eq. (13-11) and Table 12-4. We see that $Q_r \hat{J}_z^{\,2}$ and $Q_r(\hat{J}_x^{\,2} + \hat{J}_y^{\,2})$ are totally symmetric so

$$\mu^{\mathrm{e}}_{zz} a_r^{zz} \mu^{\mathrm{e}}_{zz} \neq 0 \quad \text{and} \quad \mu^{\mathrm{e}}_{xx} a_r^{xx} \mu^{\mathrm{e}}_{xx} = \mu^{\mathrm{e}}_{yy} a_r^{yy} \mu^{\mathrm{e}}_{yy} \neq 0, \tag{13-54}$$

where $r = 1, 2$, or 3. Further we have

$$\Gamma(\hat{J}_z) \otimes \Gamma(\hat{J}_x, \hat{J}_y) = \Gamma(Q_{ta}, Q_{tb}) \tag{13-55}$$

and

$$\Gamma(\hat{J}_x, \hat{J}_y) \otimes \Gamma(\hat{J}_x, \hat{J}_y) \supset \Gamma(Q_{ta}, Q_{tb}), \tag{13-56}$$

where $t = 4, 5$, or 6. From a detailed consideration of the transformation properties of Q_{ta} and Q_{tb} (or of Q_t^+ and Q_t^-) in Table 12-4 we determine that the centrifugal coupling operator

$$[Q_{ta}(\hat{J}_x \hat{J}_z + \hat{J}_z \hat{J}_x) + Q_{tb}(\hat{J}_y \hat{J}_z + \hat{J}_z \hat{J}_y)] \tag{13-57}$$

is totally symmetric. Thus

$$\begin{aligned} \mu^{\mathrm{e}}_{xx} a_{ta}^{xz} \mu^{\mathrm{e}}_{zz} &= \mu^{\mathrm{e}}_{zz} a_{ta}^{zx} \mu^{\mathrm{e}}_{xx} = \mu^{\mathrm{e}}_{yy} a_{tb}^{yz} \mu^{\mathrm{e}}_{zz} \\ &= \mu^{\mathrm{e}}_{zz} a_{tb}^{zy} \mu^{\mathrm{e}}_{yy} (= \mu^{\mathrm{e}}_{xx} a_t^{xz} \mu^{\mathrm{e}}_{zz}, \text{ say}) \neq 0 \end{aligned} \tag{13-58}$$

in CH_3F where $t = 4$, 5, or 6. We can write the appropriate centrifugal distortion term as

$$-\frac{1}{4}\mu^{\mathrm{e}}_{xx}a^{xz}_{t}\mu^{\mathrm{e}}_{zz}[Q_t^{-}(\hat{J}_{\mathrm{m}}{}^{+}\hat{J}_z + \hat{J}_z\hat{J}_{\mathrm{m}}{}^{+}) + Q_t^{+}(\hat{J}_{\mathrm{m}}{}^{-}\hat{J}_z + \hat{J}_z\hat{J}_{\mathrm{m}}{}^{-})]. \tag{13-59}$$

Similarly

$$\begin{aligned}\mu^{\mathrm{e}}_{xx}a^{xy}_{tb}\mu^{\mathrm{e}}_{yy} &= \mu^{\mathrm{e}}_{yy}a^{yx}_{tb}\mu^{\mathrm{e}}_{xx} = \mu^{\mathrm{e}}_{yy}a^{yy}_{ta}\mu^{\mathrm{e}}_{yy} \\ &= -\mu^{\mathrm{e}}_{xx}a^{xx}_{ta}\mu^{\mathrm{e}}_{xx} \ \ (= -\mu^{\mathrm{e}}_{xx}a^{xx}_{t}\mu^{\mathrm{e}}_{xx},\ \text{say}) \neq 0\end{aligned} \tag{13-60}$$

and the appropriate non-vanishing centrifugal distortion term can be written as

$$-\frac{1}{4}\mu^{\mathrm{e}}_{xx}a^{xx}_{t}\mu^{\mathrm{e}}_{xx}[Q_t^{+}(\hat{J}_{\mathrm{m}}{}^{+})^2 + Q_t^{-}(\hat{J}_{\mathrm{m}}{}^{-})^2], \tag{13-61}$$

where $t = 4$, 5, or 6.

The symmetric Coriolis coupling operators are [where the terms arising from the antisymmetry of the ζ coefficients, see Eq. (11-80), are to be understood]

$$(Q_r\hat{P}_{sa}\hat{J}_y - Q_r\hat{P}_{sb}\hat{J}_x), \tag{13-62}$$

$$(Q_{sa}\hat{P}_{tb} - Q_{sb}\hat{P}_{ta})\hat{J}_z, \tag{13-63}$$

and

$$(Q_{sa}\hat{P}_{ta} - Q_{sb}\hat{P}_{tb})\hat{J}_y + (Q_{sa}\hat{P}_{tb} + Q_{sb}\hat{P}_{ta})\hat{J}_x, \tag{13-64}$$

so that the nonvanishing Coriolis coupling coefficients are

$$\zeta^{y}_{r,sa} = -\zeta^{x}_{r,sb}(= \zeta^{y}_{r,s}, \text{say}), \tag{13-65}$$

$$\zeta^{z}_{sa,tb} = -\zeta^{z}_{sb,ta}(= \zeta^{z}_{s,t}, \text{say}), \tag{13-66}$$

and

$$\zeta^{y}_{sa,ta} = -\zeta^{y}_{sb,tb} = \zeta^{x}_{sa,tb} = \zeta^{x}_{sb,ta}(= \zeta^{y}_{s,t}, \text{say}), \tag{13-67}$$

where $r = 1, 2$, or 3 and $s, t = 4, 5$, or 6 [s can equal t in Eq. (13-66) but not in Eq. (13-67) because of the antisymmetry of the ζ coefficients]. The nonvanishing Coriolis coupling terms [note the minus sign in Eq. (13-7)] can be written

$$-(i/2)\mu^{\mathrm{e}}_{yy}\zeta^{y}_{r,s}Q_r(\hat{P}_s{}^{+}\hat{J}_{\mathrm{m}}{}^{-} - \hat{P}_s{}^{-}\hat{J}_{\mathrm{m}}{}^{+}), \tag{13-68}$$

$$-(i/2)\mu^{\mathrm{e}}_{zz}\zeta^{z}_{s,t}(Q_s{}^{+}\hat{P}_t{}^{-} - Q_s{}^{-}\hat{P}_t{}^{+})\hat{J}_z, \tag{13-69}$$

and

$$-(i/2)\mu^{e}_{yy}\zeta^{y}_{s,t}(Q_s{}^{-}\hat{P}_t{}^{-}\hat{J}_{\mathrm{m}}{}^{-} - Q_s{}^{+}\hat{P}_t{}^{+}\hat{J}_{\mathrm{m}}{}^{+}), \tag{13-70}$$

where $r = 1, 2$, or 3 and $s, t = 4, 5$, or 6 [$s \neq t$ in Eq. (13-70)].

The term in Eq. (13-68) causes a Coriolis resonance between the ν_2 (of A_1 symmetry) and ν_5 (of E symmetry) fundamental levels of methyl halides. The interaction matrix elements have $\Delta k = \Delta l_5 = \pm 1$ [see Eq. (13-43)]. In CH_3F the ν_2 and ν_5 vibrational energies are 1459.4 and 1467.8 cm^{-1}, respectively, so that the interaction between the rovibrational levels in the two vibrational states is strong and gives rise to the irregular looking spectrum shown in Fig. 13-4 [Papoušek, Papoušková, Ogilvie, Pracna, Civiš, and Winnewisser (1992)].

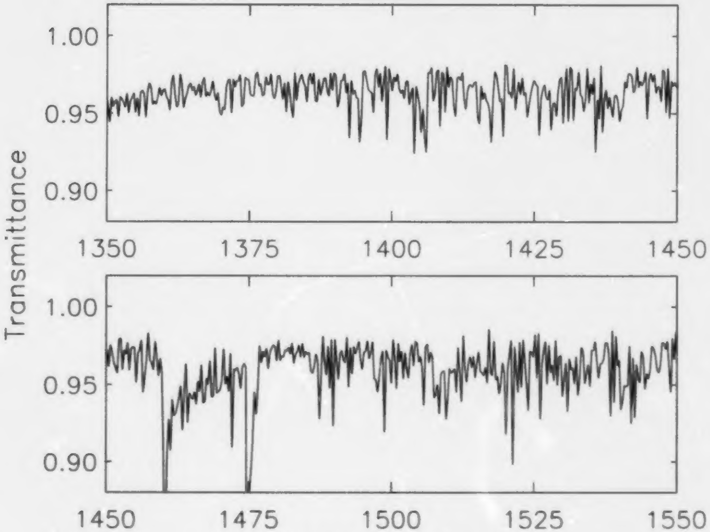

Fig. 13-4. The ν_2 and ν_5 bands of CH_3F [after Papoušek, Papoušková, Ogilvie, Pracna, Civiš, and Winnewisser (1992)]. The upper states of the transitions result from a strong Coriolis resonance between the ν_2 and ν_5 basis states caused by the operator in Eq. (13-68). The prominent feature near 1460 cm^{-1} can be described as the Q branch of the ν_2 band [consisting of transitions with $\Delta J = \Delta K = 0$, see Chapter 14], and the prominent feature at 1475 cm^{-1} can be described as a Q branch of the ν_5 band with $K = 1 \leftarrow 0$.

Anharmonicity perturbations mix states of the same symmetry Γ_{vib} in the MS group, with selection rules on the vibrational quantum numbers that can be easily deduced from the results in Tables 11-2 and 11-3. For example, for the CH_3F molecule (see Problem 13-3) the following terms are among the nonvanishing cubic and quartic anharmonicity terms

$$\begin{aligned} V_{\text{anh}}^{(1)} &= \Phi_{1123} Q_1{}^2 Q_2 Q_3/2, \\ V_{\text{anh}}^{(2)} &= \Phi_{145} Q_1 (Q_4{}^+ Q_5{}^- + Q_4{}^- Q_5{}^+)/2, \\ V_{\text{anh}}^{(3)} &= \Phi_{456} (Q_4{}^+ Q_5{}^+ Q_6{}^+ + Q_4{}^- Q_5{}^- Q_6{}^-)/2. \end{aligned} \tag{13-71}$$

The nonvanishing matrix elements of these terms can be determined from the results in Eq. (11-125) and in Tables 11-2 and 11-3. We determine that $V_{\text{anh}}^{(1)}$ has nonvanishing matrix elements between vibrational states with the selection rules

$$\Delta v_1 = 0, \pm 2, \qquad \Delta v_2 = \pm 1, \qquad \Delta v_3 = \pm 1. \tag{13-72}$$

$V_{\text{anh}}^{(2)}$ has nonvanishing matrix elements with selection rules

$$\Delta v_1 = \pm 1, \quad \Delta v_4 = \pm 1, \quad \Delta v_5 = \pm 1, \quad \Delta l_4 = -\Delta l_5 = \pm 1, \tag{13-73}$$

and $V_{\text{anh}}^{(3)}$ has nonvanishing matrix elements with selection rules

$$\Delta v_4 = \pm 1, \quad \Delta v_5 = \pm 1, \quad \Delta v_6 = \pm 1, \quad \Delta l_4 = \Delta l_5 = \Delta l_6 = \pm 1. \tag{13-74}$$

These equations satisfy Eqs. (13-44) and (13-45).

The centrifugal distortion perturbation terms [Eq. (13-6)], like the Coriolis perturbation terms, mix states in which both the vibrational and rotational quantum numbers change, although the vibration-rotation species Γ_{rv} must be maintained. The selection rules on the vibration and rotation quantum numbers can be derived from the results in Tables 11-1 to 11-3. For example, in the CH_3F molecule among the nonvanishing centrifugal distortion terms [see Eq. (13-61)] is

$$T_{\text{cent}}^{(1)} = -\frac{1}{4} \mu_{xx}^{\text{e}} a_4^{xx} \mu_{xx}^{\text{e}} [Q_4{}^+ (\hat{J}_{\text{m}}{}^+)^2 + Q_4{}^- (\hat{J}_{\text{m}}{}^-)^2]. \tag{13-75}$$

This term mixes rotation-vibration states according to the selection rules

$$\Delta v_4 = \pm 1$$

with

$$\Delta l_4 = +1 \quad \text{and} \quad \Delta k = -2 \text{ or } \Delta l_4 = -1 \quad \text{and} \quad \Delta k = +2, \tag{13-76}$$

which satisfies Eq. (13-43).

Clearly the first term in the centrifugal distortion term of Eq. (13-6) will mix vibration-rotation states with vibrational quantum numbers that differ by one because Q_r occurs in it. For a rigid molecule such as we are considering here none of the vibrational energy separations will be of the order of a rotational energy separation, and perturbation theory can reasonably be used to treat the effect of this term (unless $a_r^{\alpha\beta}$ is anomalously large). The second term in Eq. (13-6) has a coefficient of $Q_r Q_s \hat{J}_\alpha \hat{J}_\beta$ that is usually an order of magnitude smaller than the coefficient of $Q_r \hat{J}_\alpha \hat{J}_\beta$ in the first term. However the second term couples states that differ by one unit in two vibrational quantum numbers, i.e., the levels of the states $v_r = 1$ and $v_s = 1$ can be coupled by this term; it is possible for such coupled states to be close in energy (i.e., in resonance) and for the perturbation treatment of the effect of T_{cent} to fail. For example, in trans diimide the centrifugal distortion term

$$\frac{3}{4}\mu^e_{aa}a_2^{aa}\mu^e_{aa}a_3^{aa}\mu^e_{aa}Q_2Q_3\hat{J}_a{}^2 \tag{13-77}$$

is nonvanishing [see Eq. (13-27)] and the $v_2 = 1$ and $v_3 = 1$ states that are mixed by this term are close in energy. As a result of the resonance between levels that are coupled by this term, it can have a significant effect.

The selection rules on the vibrational and rotational quantum numbers for allowed Coriolis coupling interactions can likewise be obtained from the results in Tables 11-1 to 11-3. From Eq. (13-70) we see that a nonvanishing Coriolis coupling term in CH_3F is

$$-(i/2)\mu^e_{yy}\zeta^y_{4,5}[Q_4{}^-\hat{P}_5{}^-\hat{J}_m{}^- - Q_4{}^+\hat{P}_5{}^+\hat{J}_m{}^+] \tag{13-78}$$

and the selection rules for states to be coupled by this term are

$$\Delta v_4 = \pm 1 \qquad \text{and} \qquad \Delta v_5 = \pm 1$$

with

$$\Delta l_4 = \Delta l_5 = -\Delta k = \pm 1. \tag{13-79}$$

Another nonvanishing Coriolis coupling term for CH_3F is

$$-(i/2)\mu^e_{zz}\zeta^z_{s,s}(Q_s{}^+\hat{P}_s{}^- - Q_s{}^-\hat{P}_s{}^+)\hat{J}_z, \tag{13-80}$$

where $s = 4, 5$, or 6, and this couples states with the selection rules

$$\Delta v_s = 0, \pm 2 \qquad \text{and} \qquad \Delta l_s = \Delta k = 0. \tag{13-81}$$

Equations (13-79) and (13-81) satisfy Eq. (13-43). The terms in Eq. (13-80) have nonvanishing diagonal matrix elements and produce an important first order Coriolis splitting of levels having the same quantum number labels v_s and K.

The* ($\pm l$) *quantum number label: The Coriolis coupling perturbation

$$-(i/2)\mu^e_{zz}\zeta^z_{4,4}(Q_4{}^+\hat{P}_4{}^- - Q_4{}^-\hat{P}_4{}^+)\hat{J}_z \tag{13-82}$$

has nonvanishing first order matrix elements (i.e., $\Delta k = 0$ and $\Delta v_4 = \Delta l_4 = 0$) within any rotation-vibration state for which l_4 and k are nonzero. Using

Eq. (13-82) together with the expressions for the matrix elements of the two-dimensional harmonic oscillator (see Table 11-3) we deduce that the first order energy of states for which $v_5 = v_6 = 0$ is given by (in cm^{-1})

$$E_{\mathrm{rv}} = E^0_{\mathrm{rv}} - 2Ak\zeta^z_{4,4}l_4, \tag{13-83}$$

where E^0_{rv} is the rigid rotor harmonic oscillator energy which has a $2(v_4 + 1)$-fold degeneracy if $k \neq 0$ [see also Eq. (13-129) which follows]. As a result the pair of levels with $kl_4 > 0$ [i.e., $(k, l_4) = \pm(|k|, |l_4|)$] have energy

$$E_{\mathrm{rv}} = E^0_{\mathrm{rv}} - 2AK\zeta^z_{4,4}|l_4| \tag{13-84}$$

and the pair of levels with $kl_4 < 0$ [i.e., $(k, l_4) = \pm(|k|, -|l_4|)$] have energy

$$E_{\mathrm{rv}} = E^0_{\mathrm{rv}} + 2AK\zeta^z_{4,4}|l_4|, \tag{13-85}$$

where $K = |k|$. Since the splitting is first order it is useful to have an extra label to distinguish the level with energy given by Eq. (13-84) from that with energy given by Eq. (13-85) for a given pair of $(|k|, |l_4|)$ values. This label is the $(\pm l)$ label: one level is called the $(+l)$ level and the other is called the $(-l)$ level. The sign of the $(\pm l)$ label depends on the relative and absolute values of k and g_{v} and is given by [Hoy and Mills (1973)]

$$\mathrm{sgn}[k \sin(2\pi g_{\mathrm{v}}/3)]. \tag{13-86}$$

Levels for which Eq. (13-86) is positive are $(+l)$ levels and levels for which Eq. (13-86) is negative are $(-l)$ levels. In the $v_4 = 1$ state $g_{\mathrm{v}} = l_4 = \pm 1$ and we see that levels with energy given by Eq. (11-123) are the $(+l)$ levels and those with energy given by Eq. (13-85) are the $(-l)$ levels. As another example, in the $v_4 = 2$ state of $\mathrm{CH_3F}$ the pair of levels $k = +K, l_4 = +2$ and $k = -K, l_4 = -2$, with a first order energy shift of $-4AK\zeta^z_{4,4}$, are the $(-l)$ pair, and the pair $k = -K, l_4 = +2$ and $k = +K, l_4 = -2$, with a first order energy shift of $+4AK\zeta^z_{4,4}$, are the $(+l)$ pair. In the $v_4 = 2$ state the pair of $l_4 = 0$ levels do not suffer a first order Coriolis splitting and the $(\pm l)$ label is not used for them.

In general for a vibrational state of $\mathrm{CH_3F}$ that has species E, the rotation-vibration species of the $(+l)$ and $(-l)$ levels depend on K as shown in Table 13-3. It is this symmetry that determines the $(\pm l)$ label and not the relative signs of k and l_4 (compare the $v_4 = 1$ and $v_4 = 2$ examples discussed above for $\mathrm{CH_3F}$). To extend the $(\pm l)$ label to degenerate vibronic states we use g_{ve} instead of g_{v} in Eq. (13-86), and to extend it to other symmetric tops we rewrite the equation as [Hoy and Mills (1973)]

$$\mathrm{sgn}[k \sin(2\pi g_{\mathrm{ve}}/n)] \tag{13-87}$$

where n is the order of the primary axis of symmetry in the molecule.

Table 13-3

Symmetry of ($\pm l$) levels of CH_3F in an E vibronic state with $K > 0$[a]

	Γ_{rve}	
K :	$(+l)$	$(-l)$
$3n+1$:	$A_1 \oplus A_2$	E
$3n+2$:	E	$A_1 \oplus A_2$
$3n+3$:	E	E

[a] n is a nonnegative integer; $K = |k|$.

13.2.3 Spherical top molecules

Examples of spherical top molecules are CH_4, SF_6, and C_{60}. We calculate the spin statistical weights of these molecules in Chapter 8. The MS group of CH_4 is the the tetrahedral group $\boldsymbol{T}_d(M)$ [Table A-14], the MS group of SF_4 is the the octahedral group $\boldsymbol{O}_h(M)$ [Table A-15], and the MS group of C_{60} is the the icosahedral group $\boldsymbol{I}_h(M)$ [Table A-16]. The rotation-vibration Hamiltonian given in Eqs. (10-150)-(10-154) together with Eq. (10-143) applies to spherical top molecules just as it applies to asymmetric top molecules and symmetric top molecules. The molecular rotation group of a spherical top molecule is $\boldsymbol{K}$(mol) [Section 12.6], which contains the rotations of the molecule about any axis that has a definite orientation within the molecule fixed axis system. The group $\boldsymbol{K}$(mol) is such a useful near symmetry group for a spherical top that it has proved advantageous to reformulate the rotation-vibration Hamiltonian in a manner based on $\boldsymbol{K}$(mol) symmetry. As usual the Hamiltonian is expressed as the sum of terms each of which is totally symmetric in the MS group. But now these terms are themselves expressed as the sum of terms each of which transforms irreducibly in $\boldsymbol{K}$(mol);[1] each of these terms being the contraction of two spherical tensor operators that transform irreducibly in $\boldsymbol{K}$(mol) [see the last paragraph of Section 10.3.1].[2] The reformulation makes the rotation-vibration theory of spherical top molecules appear extremely different from that of asymmetric tops or symmetric tops, and we give a summary of this theory.

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[1] See Section 7.3.2; the two groups $\boldsymbol{K}$(spatial) and $\boldsymbol{K}$(mol) are isomorphic and we use the same names for the irreducible representations.

[2] If the group $\boldsymbol{K}$(mol) were a true symmetry group of the molecular Hamiltonian we would only need to construct terms having symmetry $D^{(0)}$ in $\boldsymbol{K}$(mol), but since it is a near symmetry group terms of any symmetry $D^{(\omega)}$ can be nonvanishing; however, we can expect that terms of symmetry $D^{(0)}$ in $\boldsymbol{K}$(mol) will be the dominant ones.

In Chapter 12 [see Table 12-3 on page 275] we describe how the rotational basis functions of a spherical top molecule are classified in the MS group. This is done by noting that the set of symmetric top functions $|J,k,m\rangle$, $k = -J, -J+1, \ldots, J$, transform as the irreducible representation $D^{(J)}$ of $\boldsymbol{K}$(mol). The symmetries in the MS group are determined using the correlation from $\boldsymbol{K}$(mol) to the MS group. For a spherical top the terms in the rotation-vibration Hamiltonian that are totally symmetric in the MS group are determined in a similar way [Hecht (1960a, 1960b)]:

- We form linear combinations of the normal coordinates Q_r, their conjugate momenta $\hat{P}_r$, and the molecule fixed components $(\hat{J}_x, \hat{J}_y, \hat{J}_z)$ that transform irreducibly in $\boldsymbol{K}$(mol). A vibrational operator (i.e., an operator constructed from Q_r and $\hat{P}_r$) transforming according to the σ_v'th row of the irreducible representation $D^{(\omega_v)}$ of $\boldsymbol{K}$(mol) is denoted $T_v^{(\omega_v,\sigma_v)}$. A rotational operator (constructed from $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$) transforming according to the σ_r'th row of the irreducible representation $D^{(\omega_r)}$ of $\boldsymbol{K}$(mol) is denoted $T_r^{(\omega_r,\sigma_r)}$. Examples of the operators $T_v^{(\omega_v,\sigma_v)}$ and $T_r^{(\omega_r,\sigma_r)}$ are given below.

- We form rotation-vibration operators by coupling the operators $T_v^{(\omega_v,\sigma_v)}$ and $T_r^{(\omega_r,\sigma_r)}$ in a manner similar to that given for angular momentum eigenfunctions in Eq. (10-98):

$$T_{rv}^{(\omega,\sigma)} = \sum_{\sigma_v,\sigma_r} (-1)^{\omega_v-\omega_r+\sigma} \sqrt{2\omega+1} \begin{pmatrix} \omega_v & \omega_r & \omega \\ \sigma_v & \sigma_r & -\sigma \end{pmatrix} T_v^{(\omega_v,\sigma_v)} T_r^{(\omega_r,\sigma_r)}. \tag{13-88}$$

  The operator $T_{rv}^{(\omega,\sigma)}$ transforms according to the σ'th row of the irreducible representation $D^{(\omega)}$ of $\boldsymbol{K}$(mol). The rotation-vibration Hamiltonian is Hermitian, and is invariant under time reversal [see Chapter 7], so that in each term $T_{rv}^{(\omega,\sigma)}$ the total power of momentum operators [$\hat{P}_r$ and $\hat{J}_\alpha$] must be even.

- We form the linear combinations of $T_{rv}^{(\omega,\sigma)}$ that are totally symmetric in the MS group. For example, for $\boldsymbol{T}_d$(M) [Table A-14] molecules, $T_{rv}^{(\omega,\sigma)}$ operators with $\omega \le 8$ give rise to the following terms having A_1 symmetry in $\boldsymbol{T}_d$(M) [Jahn (1938a, 1938b), Hecht (1960a, 1960b), Ozier (1974)]

$$\begin{aligned}
T_{A_1}^{(0)} &= T_{rv}^{(0,0)}, \\
T_{A_1}^{(4)} &= \sqrt{70}\, T_{rv}^{(4,0)} + 5\left(T_{rv}^{(4,4)} + T_{rv}^{(4,-4)}\right), \\
T_{A_1}^{(6)} &= \sqrt{14}\, T_{rv}^{(6,0)} - 7\left(T_{rv}^{(6,4)} + T_{rv}^{(6,-4)}\right), \\
T_{A_1}^{(8)} &= T_{rv}^{(8,0)} + \sqrt{\frac{28}{198}}\left(T_{rv}^{(8,4)} + T_{rv}^{(8,-4)}\right) + \sqrt{\frac{65}{198}}\left(T_{rv}^{(8,8)} + T_{rv}^{(8,-8)}\right).
\end{aligned} \tag{13-89}$$

The rotation-vibration Hamiltonian is written as a linear combination of terms such as those given in Eq. (13-89). The expansion coefficients are normally determined in fittings to experimental data.

Starting from the three irreducible spherical tensor operators [see Eq. (8) of Robiette, Gray, and Birss (1976)[3]]

$$\begin{aligned} T_{\mathrm{r}}^{(1,\pm1)} &= \pm \hat{J}_{\mathrm{m}}{}^{\pm}/\sqrt{2} \\ T_{\mathrm{r}}^{(1,0)} &= -\hat{J}_z , \end{aligned} \tag{13-90}$$

rotational operators of higher ranks are constructed by repeated use of the expression

$$T_{\mathrm{r}}^{(\omega,\sigma)} = \sum_{\sigma_{\mathrm{r}}',\sigma_{\mathrm{r}}''} (-1)^{\omega_{\mathrm{r}}'-\omega_{\mathrm{r}}''+\sigma} \sqrt{2\omega+1} \begin{pmatrix} \omega_{\mathrm{r}}' & \omega_{\mathrm{r}}'' & \omega \\ \sigma_{\mathrm{r}}' & \sigma_{\mathrm{r}}'' & -\sigma \end{pmatrix} T_{\mathrm{r}}^{(\omega_{\mathrm{r}}',\sigma_{\mathrm{r}}')} T_{\mathrm{r}}^{(\omega_{\mathrm{r}}'',\sigma_{\mathrm{r}}'')} , \tag{13-91}$$

which is analogous to Eq. (13-88). The irreducible spherical tensor operators given Eq. (13-90) are changed in sign relative to analogous operators introduced in Chapter 14 [see, for example, Eq. (14-13)]. The reason for the sign change is discussed in Section 20.1 of Papoušek and Aliev (1982), and it occurs because the molecule fixed components $(\hat{J}_x, \hat{J}_y, \hat{J}_z)$ of the angular momentum obey the commutation relations of Eq. (10-92), and the three reversed components [see Van Vleck (1951)] $(-\hat{J}_x, -\hat{J}_y, -\hat{J}_z)$ satisfy the commutation relations of Eq. (10-90). Using the reversed components in Eq. (13-90) leads to a simplification in the determination of the matrix elements of rotational operators because standard angular momentum theory, in particular the Wigner-Eckart theorem [see Section 10.3], can be employed without modification. In their Appendix A, Robiette, Gray, and Birss (1976) list rotational operators with ranks 2, 3, and 4 determined from Eq. (13-91).

One important difference between spherical top molecules on one hand and asymmetric and symmetric top molecules on the other is that spherical top molecules have triply degenerate normal coordinates. For example, methane has the normal modes ν_1 (A_1), ν_2 (E), ν_3 (F_2), and ν_4 (F_2) where we give the symmetry in $\boldsymbol{T}_{\mathrm{d}}(\mathrm{M})$ of each normal mode in parentheses [Eq. (12-31)]. The triply degenerate normal modes are described by normal coordinates (Q_{tx}, Q_{ty}, Q_{tz}) with conjugate momenta $(\hat{P}_{tx}, \hat{P}_{ty}, \hat{P}_{tz})$. For the normal coordinates of a doubly degenerate vibration it is necessary to adopt a convention for their transformation properties in the MS group [see Section 12.1.2] A similar convention must be adopted for the coordinates (Q_{tx}, Q_{ty}, Q_{tz}) here. For symmetric top molecules the convention is that proposed by di Lauro and Mills (1966), but there is no similar generally accepted convention for spherical top molecules. For CH_4 an obvious choice would be to let (Q_{tx}, Q_{ty}, Q_{tz}), $t = 3$ or 4, transform as (T_x, T_y, T_z) since these three coordinates have F_2 symmetry in $\boldsymbol{T}_{\mathrm{d}}(\mathrm{M})$.

For a triply degenerate normal mode ν_t the harmonic oscillator eigenfunctions are written $\Phi_{v_t l_t n_t}$. The l_t and n_t are the quantum numbers associated with the vibrational angular momentum $\hat{\boldsymbol{l}}_t$ of ν_t. The z-component of $\hat{\boldsymbol{l}}_t$ is given by [cf. Eq. (11-151)]

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[3] Note that their $J_{\pm} = \hat{J}_{\mathrm{m}}{}^{\mp}$

$$\hat{l}_{tz} = Q_{tx}\hat{P}_{ty} - Q_{ty}\hat{P}_{tx} \tag{13-92}$$

and the expressions for $\hat{l}_{tx}$ and $\hat{l}_{ty}$ are obtained by cyclic permutation of xyz in Eq. (13-92). The harmonic oscillator eigenfunction Ψ_{v_t,l_t,n_t} satisfies the eigenvalue equations

$$\hat{\boldsymbol{l}}_t{}^2\Psi_{v_t,l_t,n_t} = l_t(l_t+1)\hbar^2\Psi_{v_t,l_t,n_t} \tag{13-93}$$

and

$$\hat{l}_{tz}\Psi_{v_t,l_t,n_t} = n_t\hbar\Psi_{v_t,l_t,n_t}. \tag{13-94}$$

Comparison of Eqs. (13-93) and (13-94) with Eqs. (10-95), (10-96), (11-170), and (11-171) shows that the functions Ψ_{v_t,l_t,n_t} can be viewed as being standard angular momentum eigenfunctions describing the vibrational angular momentum in the triply degenerate normal mode.

As examples of vibrational operators $T_{\mathrm{v}}^{(\omega_{\mathrm{v}},\sigma_{\mathrm{v}})}$, we consider the irreducible spherical tensor operators that can be constructed from (Q_{tx}, Q_{ty}, Q_{tz}), $(\hat{P}_{tx}, \hat{P}_{ty}, \hat{P}_{tz})$, and from the components of $\hat{\boldsymbol{l}}_t$ for a $\boldsymbol{T}_{\mathrm{d}}(\mathrm{M})$ molecule like CH_4. Robiette, Gray, and Birss (1976) give expressions for the vibrational operators of rank 1 and 2. The operators of rank 1 are given by

$$\begin{aligned} T_{\mathrm{v}}^{(1,\pm1)} &= \mp\left(\hat{l}_{tx} \pm i\hat{l}_{ty}\right)/\sqrt{2}, \\ T_{\mathrm{v}}^{(1,0)} &= \hat{l}_{tz}. \end{aligned} \tag{13-95}$$

The operators of rank 2 are expressed in terms of the dimensionless operators

$$q_{t\alpha} = \gamma_t^{1/2}Q_{t\alpha} \text{ and } \hat{p}_{t\alpha} = \gamma_t^{-1/2}\hat{P}_{t\alpha}/\hbar, \tag{13-96}$$

with $\alpha = x, y, z$ and [Eq. (11-106)]

$$\hbar\gamma_t = 2\pi c\omega_t, \tag{13-97}$$

where ω_t is the harmonic vibrational wavenumber for the normal mode ν_t. The vibrational operators of rank 2 are

$$\begin{aligned} T_{\mathrm{v}}^{(2,\pm2)} &= \left[(q_{tx} \pm iq_{ty})^2 + (\hat{p}_{tx} \pm i\hat{p}_{ty})^2\right]/4 \\ T_{\mathrm{v}}^{(2,\pm1)} &= \mp\left[(q_{tx} \pm iq_{ty})\,q_{tz} + (\hat{p}_{tx} \pm i\hat{p}_{ty})\,\hat{p}_{tz}\right]/2 \\ T_{\mathrm{v}}^{(2,0)} &= \left[3\left(q_{tz}^2 + \hat{p}_{tz}^2\right) - \sum_{\alpha}\left(q_{t\alpha}^2 + \hat{p}_{t\alpha}^2\right)\right]/(2\sqrt{6}). \end{aligned} \tag{13-98}$$

These operators and those in Eq. (13-95) are coupled [in an expression obtained by replacing 'r' by 'v' in Eq. (13-91)] to produce further irreducible spherical tensor operators $T_{\mathrm{v}}^{(\omega_{\mathrm{v}},\sigma_{\mathrm{v}})}$. In their Section 20, Papoušek and Aliev (1982) consider $\boldsymbol{T}_{\mathrm{d}}(\mathrm{M})$ molecules and give many examples of operators $T_{\mathrm{r}}^{(\omega_{\mathrm{r}},\sigma_{\mathrm{r}})}$ [which they call $\boldsymbol{R}(\omega_{\mathrm{r}}\sigma_{\mathrm{r}})$], $T_{\mathrm{v}}^{(\omega_{\mathrm{v}},\sigma_{\mathrm{v}})}$ [which they call $\boldsymbol{V}(\omega_{\mathrm{v}}\sigma_{\mathrm{v}})$], and operators $T_{A_1}^{(\omega)}$ determined from Eqs. (13-88) and (13-89) [Papoušek and Aliev (1982) call these operators $\boldsymbol{T}(\omega_{\mathrm{v}}\omega_{\mathrm{r}}\omega)$; such an operator is obtained in Eq. (13-89) from operators $T_{\mathrm{rv}}^{(\omega,\sigma)}$ ($\sigma = -\omega, \ldots, \omega$), which in turn are given by Eqs. (13-88) in terms of two sets of operators $T_{\mathrm{r}}^{(\omega_{\mathrm{r}},\sigma_{\mathrm{r}})}$ and $T_{\mathrm{v}}^{(\omega_{\mathrm{v}},\sigma_{\mathrm{v}})}$]. Many of the operators given by Papoušek and Aliev (1982) involve powers of $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ higher than two. Such terms are not present in the kinetic energy operator for rotation and vibration given by Eqs. (10-150)-(10-154), but they are present in the effective rotational Hamiltonian (the ***Watsonian***) for a particular vibrational state of a spherical top molecule. The Watsonian is discussed in Section 13.2.4 which follows.

Not only the rotation-vibration Hamiltonian, but also the rotation-vibration basis functions of a spherical top molecule are rewritten so as to take into account $\boldsymbol{K}(\mathrm{mol})$ symmetry. The total vibrational angular momentum $\hat{\boldsymbol{l}}$ from the triply degenerate normal modes is defined as

$$\hat{\boldsymbol{l}} = \sum_t \hat{\boldsymbol{l}}_t, \tag{13-99}$$

where the sum runs over all triply degenerate normal modes of the molecule. The CH_4 molecule has $\hat{\boldsymbol{l}} = \hat{\boldsymbol{l}}_3 + \hat{\boldsymbol{l}}_4$. The vibrational basis functions involving the triply degenerate normal modes for a spherical top molecule are chosen so that they are eigenfunctions of $\hat{\boldsymbol{l}}^2$ and its z-component $\hat{l}_z$ with eigenvalues $l(l+1)\hbar^2$ and $n\hbar$, respectively. Such eigenfunctions are obtained by coupling the functions $|v_t, l_t, n_t\rangle \equiv \Psi_{v_t,l_t,n_t}$, which satisfy Eqs. (13-93) and (13-94), by means of Eq. (10-98). The molecule fixed components of the angular momenta $\hat{\boldsymbol{l}}_t$ obey commutation relations analogous to Eq. (10-90) [see, for example, Eq. (20.1.4) of Papoušek and Aliev (1982)], e.g.

$$\hat{l}_{tx}\hat{l}_{ty} - \hat{l}_{ty}\hat{l}_{tx} = i\hat{l}_{tz}. \tag{13-100}$$

Consequently, Eq. (10-98) can be used without modification to couple these angular momenta. The coupled vibrational basis functions can be written as $|V, L, l, n\rangle$, where use V as a shorthand notation for all v_t quantum numbers, and L is used as a shorthand notation for all l_t quantum numbers, including those associated with the doubly degenerate normal modes. The possible values of l are determined from the individual l_t quantum numbers as discussed in connection with Eq. (10-98). For CH_4, l can assume the values $|l_3 - l_4|$, $|l_3 - l_4| + 1$, $\ldots$, $l_3 + l_4$. The quantum number n assumes the values $-l$, $-l + 1$, $\ldots$, l.

The rotation-vibration basis functions for a spherical top molecule are often chosen to be eigenfunctions of the operator $\hat{\boldsymbol{R}}^2$ where

$$\hat{\boldsymbol{R}} = \hat{\boldsymbol{J}} - \hat{\boldsymbol{l}}. \tag{13-101}$$

Such functions are obtained by coupling of the $|V, L, l, n\rangle$ functions, which are eigenfunctions of $\hat{l}^2$ and $\hat{l}_z$, with symmetric top functions $|J, k, m\rangle$, which are eigenfunctions of $\hat{\boldsymbol{J}}^2$ and $\hat{J}_z$. However, we cannot apply Eq. (10-98) in this case. This is because $(\hat{J}_x, \hat{J}_y, \hat{J}_z)$ obey the commutation relations of Eq. (10-92), whereas $(\hat{l}_x, \hat{l}_y, \hat{l}_z)$ satisfy the commutation relations of Eq. (10-90). Brown and Howard (1976) have shown that the correct coupled function is given by

$$|V, L, J, l, R, k_R, m\rangle = \sum_{k,n} (-1)^{R-l+k} \sqrt{2R+1} \begin{pmatrix} J & l & R \\ k & -n & -k_R \end{pmatrix} \times |V, L, l, n\rangle |J, k, m\rangle . \qquad (13\text{-}102)$$

The function $|V, L, J, l, R, k_R, m\rangle$ is a simultaneous eigenfunction of $\hat{\boldsymbol{R}}^2$ [with eigenvalue $R(R+1)\hbar^2$], $\hat{R}_z$ [with eigenvalue $k_R\hbar$], $\hat{\boldsymbol{J}}^2$ [with eigenvalue $J(J+1)\hbar^2$], $\hat{J}_\zeta$ [with eigenvalue $m\hbar$], and $\hat{l}^2$ [with eigenvalue $l(l+1)\hbar^2$]. The allowed values for R are $|J-l|, |J-l|+1, \ldots, J+l$. The functions $|V, L, J, l, R, k_R, m\rangle$, $k_R = -R, -R+1, \ldots, R$ span the irreducible representation $D^{(R)}$ of $\boldsymbol{K}$(mol). Their symmetries in the MS group are determined by means of the correlation from $\boldsymbol{K}$(mol) to the MS group as described for rotational basis functions in Chapter 12 [see Table 12-3 on page 275].

It has been found convenient to use R when labeling the rotational levels of states in which one quantum of a triply degenerate mode ν_t is excited [see, for example, Hougen (1976)]. In such a state $l_t = 1$ [see Eq. (11-170)] and all other $l_{t'} = 0$. Therefore $l = 1$, and R takes on the values $J+1, J$, and $J-1$ as the zero order rotation-vibration wavefunctions generate the representations $D^{(J+1)}$, $D^{(J)}$, and $D^{(J-1)}$. It is possible to define a first order vibration-rotation Hamiltonian which only connects states according to the selection rule $\Delta R = 0$. Even though the complete Hamiltonian is not diagonal in R this is often a useful near quantum number for a spherical top just as G is for a symmetric top.

The expression for the rotation-vibration energy of the doubly degenerate vibrational state ν_2 of a tetrahedral AB_4 molecule is given by Herranz and Thyagarajan (1966). The ν_2 fundamental band of such a molecule is forbidden in the infrared, but it appears in the spectrum as a result of intensity stealing from the allowed ν_3 and ν_4 bands (see Chapter 14 for a discusion of forbidden bands and intensity stealing). The selection rules and intensities of the lines in such a band are also considered by Herranz and Thyagarajan (1966), and in a paper by Herranz, Morcillo and Gómez (1966) the ν_2 bands of CH_4 and CD_4 are analysed using these results.

In closing this introductory account of the rotation-vibration problem in spherical top molecules we mention the special properties of heavy spherical tops such as CF_4, SF_6, and C_{60} [see Harter and Patterson (1977,1984), Harter and Weeks (1989), and Harter (1993)]. For any spherical top molecule the zero order rotation-vibration Hamiltonian has symmetry $D^{(0)}$ in $\boldsymbol{K}$(mol) and the zero order rotation-vibration energy levels are highly degenerate. Including higher order terms, which are only invariant to the operations of the MS group [$\boldsymbol{T}_d$(M), $\boldsymbol{O}_h$(M) or $\boldsymbol{I}_h$(M) as appropriate], leads to splittings of the degeneracies. For heavy molecules these splittings can be exceedingly small and significant *clustering* of the rotation-vibration energy levels takes place. This is discussed further in the text around Eq. (13-134) below. The small splittings that arise has lead to the introduction of special terms such as *superfine splittings* to describe the situation. One interesting aspect of the clustering is that rotational levels having different nuclear spin symmetry can occur very close together in energy so that the effects of ortho-para mixing by $\hat{H}_{\text{hfs}}$, and ortho-para transitions, are observed [see Section 13.6.3 and the Bibliographical Notes on ortho-para transitions at the end of Chapter 14].

13.2.4 The contact transformed rotation-vibration Hamiltonian

The rotation-vibration Hamiltonian [see Eqs. (11-1a)-(11-1d)] can be expanded as [Aliev and Watson (1985)]

$$\hat{H}_{\text{rv}} = \sum_{m=0}^{\infty}\sum_{n=0}^{2} \hat{H}_{mn} \tag{13-103}$$

where we write the operator $\hat{H}_{mn}$ symbolically as

$$\hat{H}_{mn} = \left(Q_r, \hat{P}_r\right)^m \hat{J}_\alpha^n, \tag{13-104}$$

that is, $\hat{H}_{mn}$ contains all terms of degree m in the vibrational operators [Q_r and $\hat{P}_r$; $r = 1, 2, 3, \dots$] and of degree n in the rotational operators [$\hat{J}_\alpha$, $\alpha = x$, y and z]. Thus, the first term on the right hand side of Eq. (13-5) belongs to $\hat{H}_{30}$ and the second term to $\hat{H}_{40}$. The first term on the right hand side of Eq. (13-6) belongs to $\hat{H}_{12}$ and the second term to $\hat{H}_{22}$. The first term on the right hand side of Eq. (13-7) belongs to $\hat{H}_{21}$. With the rotation-vibration Hamiltonian considered here all nonvanishing $\hat{H}_{mn}$ terms have $n \leq 2$, whereas m can assume all non-negative values. The Hamiltonian $\hat{H}_{\text{rv}}$ is Hermitian, and is invariant under time reversal [see Chapter 7], so that in each term $\hat{H}_{mn}$ the total power of momentum operators [$\hat{P}_r$ and $\hat{J}_\alpha$] must be even.

When we discuss the eigenvalues and eigenfunctions of $\hat{H}_{\text{rv}}$, we assume them to have been obtained by diagonalization of a matrix representation of $\hat{H}_{\text{rv}}$ in a basis set of functions such as those given by Eq. (12-73). The eigenfunctions obtained from the diagonalization are expressed as linear combinations of the basis functions as given in Eq. (6-148). A direct, brute-force method for computing the eigenvalues and eigenfunctions of $\hat{H}_{\text{rv}}$ would be to diagonalize its matrix representation numerically with a computer. The matrix blocks are in principle infinitely large, and they would have to be truncated in order that the diagonalization, known as an approximate *variational calculation*, can be carried out. There are other approximate methods for diagonalizing the matrix representation of the rotation-vibration Hamiltonian which, at least in part, are carried out analytically. These are perturbation techniques as mentioned at the beginning of Chapter 9. In the traditional approach to molecular rotation-vibration theory [see Papoušek and Aliev (1982) or the review article by Aliev and Watson (1985)] the matrix representation of $\hat{H}_{\mathrm{rv}}$ is diagonalized by means of successive *contact transformations*. The contact transformation method leads to a Hamiltonian that can be directly related to the models used for interpreting experimental spectra.

In general, we obtain the eigenvalues $E_{\mathrm{rv}}^{(j)}$ and eigenfunctions $\Phi_{\mathrm{rv}}^{(j)}$ for $\hat{H}_{\mathrm{rv}}$ by solving the Schrödinger equation

$$\hat{H}_{\mathrm{rv}}\Phi_{\mathrm{rv}}^{(j)} = E_{\mathrm{rv}}^{(j)}\Phi_{\mathrm{rv}}^{(j)}, \tag{13-105}$$

where j is an index numbering the solutions. For a symmetric top molecule we construct the matrix representation of $\hat{H}_{\mathrm{rv}}$ in a basis of the zero order wavefunctions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}$ given in Eq. (12-73). By diagonalization we obtain the eigenfunctions $\Phi_{\mathrm{rv}}^{(j)}$ as

$$\Phi_{\mathrm{rv}}^{(j)} = \sum_{V,L,k} c_{V\,L\,k}^{(j)}\,\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}, \tag{13-106}$$

where the $c_{V\,L\,k}^{(j)}$ are expansion coefficients determined as eigenvector coefficients in the matrix diagonalization. We can consider the functions $\Phi_{\mathrm{rv}}^{(j)}$ to be a new basis set for constructing the matrix representation of $\hat{H}_{\mathrm{rv}}$, and in this basis set the matrix representation is diagonal. Hence we can think of the matrix diagonalization as a method of finding a basis set, in which the matrix representation of a given Hamiltonian is diagonal.

In the contact transformation method we also start out with the Hamiltonian $\hat{H}_{\mathrm{rv}}$ and the set of basis functions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}$, but here we do not change the basis set. Instead we determine a *contact transformed Hamiltonian* whose matrix representation in the given basis set is diagonal. The Schrödinger equation of Eq. (13-105) becomes

$$\hat{U}\hat{H}_{\mathrm{rv}}\hat{U}^{-1}\hat{U}\Phi_{\mathrm{rv}}^{(j)} = E_{\mathrm{rv}}^{(j)}\hat{U}\Phi_{\mathrm{rv}}^{(j)}, \tag{13-107}$$

where $\hat{U}$ is a *unitary operator* defined as

$$\hat{U} = e^{i\hat{S}}, \tag{13-108}$$

and $\hat{S}$ is a Hermitian operator;[4] the exponential of Eq. (13-108) is expressed as its Taylor series expansion

$$\hat{U} = e^{i\hat{S}} = 1 + i\hat{S} + \frac{1}{2!}\left(i\hat{S}\right)^2 + \ldots. \tag{13-109}$$

Equation (13-107) shows that the transformed Hamiltonian

$$\tilde{H}_{\mathrm{rv}} = \hat{U}\hat{H}_{\mathrm{rv}}\hat{U}^{-1} = e^{i\hat{S}}\hat{H}_{\mathrm{rv}}e^{-i\hat{S}} \tag{13-110}$$

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[4] Here $\hat{S}$ has nothing to do with electron spin.

has the same eigenvalues as $\hat{H}_{\mathrm{rv}}$, but the eigenfunctions of $\tilde{H}_{\mathrm{rv}}$, $\psi_{\mathrm{rv}}^{(j)}$ say, are obtained from those of $\hat{H}_{\mathrm{rv}}$ by the transformation

$$\psi_{\mathrm{rv}}^{(j)} = \hat{U}\Phi_{\mathrm{rv}}^{(j)} = e^{i\hat{S}}\Phi_{\mathrm{rv}}^{(j)}. \tag{13-111}$$

Both $\hat{H}$ and $\tilde{H}$ are expressed as sums of terms of diminishing order of magnitude:

$$\hat{H}_{\mathrm{rv}} = \hat{H}_0 + \lambda\,\hat{H}_1 + \lambda^2\,\hat{H}_2 + \dots \tag{13-112}$$

and

$$\tilde{H}_{\mathrm{rv}} = \tilde{H}_0 + \lambda\,\tilde{H}_1 + \lambda^2\,\tilde{H}_2 + \dots, \tag{13-113}$$

where the power of the parameter λ indicates the diminishing order of magnitude (the value of λ has no physical significance and it may be regarded as equal to 1). It is a matter of choice based on experience how one assigns the Hamiltonian terms $\hat{H}_{mn}$ to the individual order-of-magnitude expansion terms $\hat{H}_M$, $M = 0, 1, 2, \dots$, in Eq. (13-112). In the most widely used ordering scheme [Nielsen (1951); Nielsen (1959); Amat, Nielsen, and Tarrago (1971)] $\hat{H}_M$ contains the terms with $M = m + n - 2$. According to this scheme, $\hat{H}_0 = \hat{H}_{02} + \hat{H}_{20}$, so that $\hat{H}_0$ becomes the harmonic-oscillator rigid-rotor Hamiltonian given by Eq. (11-1a). Aliev and Watson (1985) discuss this and other ordering schemes.

We assume the operator $\hat{S}$ to have the same order of magnitude as $\hat{H}_1$ and to make the order-of-magnitude expansion we rewrite Eq. (13-110) as

$$\tilde{H}_{\mathrm{rv}} = e^{i\lambda\hat{S}}\hat{H}_{\mathrm{rv}}e^{-i\lambda\hat{S}}. \tag{13-114}$$

Inserting Eqs. (13-112) for $\hat{H}_{\mathrm{rv}}$ into this equation, and using the Taylor series expansion for the exponential [Eq. (13-109)], we obtain $\tilde{H}_{\mathrm{rv}}$ as a power series in λ. Equating terms of the same power of λ with those on the right hand side of Eq. (13-113) we obtain

$$\tilde{H}_0 = \hat{H}_0, \tag{13-115}$$

$$\tilde{H}_1 = \hat{H}_1 + i\left[\hat{S}, \hat{H}_0\right], \tag{13-116}$$

$$\tilde{H}_2 = \hat{H}_2 + i\left[\hat{S}, \hat{H}_1\right] - \frac{1}{2}\left[\hat{S}, \left[\hat{S}, \hat{H}_0\right]\right], \tag{13-117}$$

and so on.

After the contact transformation $\tilde{H}_0 = \hat{H}_0$, but in general for the higher order operators $\tilde{H}_M \neq \hat{H}_M$. It is necessary to choose $\hat{H}_0$ and $\hat{S}$. Normally, we choose $\hat{H}_0 = \hat{H}_{02} + \hat{H}_{20}$, and the matrix representation of this Hamiltonian is diagonal in the basis set of functions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}$. We choose the operator $\hat{S}$ so that the matrix representation of the transformed Hamiltonian $\tilde{H}_{\mathrm{rv}}$ in this basis set is as close to being diagonal as possible. As a first step we determine $\hat{S}$

so that matrix elements $\left\langle \Phi_{\rm rv}^{(V',L',J,k',m)} \middle| \tilde{H}_1 \middle| \Phi_{\rm rv}^{(V,L,J,k,m)} \right\rangle$ of the transformed, first-order operator $\tilde{H}_1$ vanish when $V' \neq V$. From Eq. (13-116) we have

$$\left\langle \Phi_{\rm rv}^{(V',L',J,k',m)} \middle| \tilde{H}_1 \middle| \Phi_{\rm rv}^{(V,L,J,k,m)} \right\rangle = \left\langle \Phi_{\rm rv}^{(V',L',J,k',m)} \middle| \hat{H}_1 \middle| \Phi_{\rm rv}^{(V,L,J,k,m)} \right\rangle$$
$$- i \left(E^{(0)}_{V',L',J,k'} - E^{(0)}_{V,L,J,k} \right) \left\langle \Phi_{\rm rv}^{(V',L',J,k',m)} \middle| \hat{S} \middle| \Phi_{\rm rv}^{(V,L,J,k,m)} \right\rangle \qquad (13\text{-}118)$$

where we have used the fact that the functions $\Phi_{\rm rv}^{(V,L,J,k,m)}$ are eigenfunctions for $\hat{H}_0$ with eigenvalues $E^{(0)}_{V,L,J,k}$. Customarily, it is assumed that the vibrational energy will be the dominating contribution to $E^{(0)}_{V,L,J,k}$, so that these energies are approximated by $E^{(0)}_V = E_{\rm vib}$, the zero order vibrational energy given by Eqs. (11-5) and (11-7). In this approximation, we deduce that for the matrix element of Eq. (13-118) to vanish, the matrix elements of $\hat{S}$ with $V' \neq V$ must be given by

$$\left\langle \Phi_{\rm rv}^{(V',L',J,k',m)} \middle| \hat{S} \middle| \Phi_{\rm rv}^{(V,L,J,k,m)} \right\rangle = -i \frac{\left\langle \Phi_{\rm rv}^{(V',L',J,k',m)} \middle| \hat{H}_1 \middle| \Phi_{\rm rv}^{(V,L,J,k,m)} \right\rangle}{E^{(0)}_{V'} - E^{(0)}_V}. \qquad (13\text{-}119)$$

If $\hat{S}$ is chosen so that its matrix elements for $V' \neq V$ are given by this equation (the matrix elements with $V' = V$ are of no importance here; they affect the second-order calculation), then the matrix elements of the transformed Hamiltonian $\tilde{H}_{\rm rv}$ with $V' \neq V$ originate in the terms $\tilde{H}_2$, $\tilde{H}_3$, $\tilde{H}_4$, ... Hence these matrix elements are expected to be smaller than the corresponding matrix elements of $\hat{H}_{\rm rv}$. Thus, the matrix representation of $\tilde{H}_{\rm rv}$ in the basis of functions $\Phi_{\rm rv}^{(V,L,J,k,m)}$ is "more diagonal" than that of $\hat{H}_{\rm rv}$.

We could apply a further contact transformation to $\tilde{H}_{\rm rv}$ to make the matrix elements of $\tilde{H}_2$ with $V' \neq V$ vanish. By applying successive contact transformations, we can in principle obtain an $\tilde{H}_{\rm rv}$ with a matrix representation in which the the off-diagonal elements are as small as we like, and the diagonal elements would represent the rotation-vibration energies. As discussed by Aliev and Watson (1985), in practice the contact transformation procedure is used to make the matrix representation of $\tilde{H}_{\rm rv}$ block diagonal. For the contact transformation procedure to be feasible, the absolute value of an off-diagonal matrix element eliminated by the transformation must be much smaller than the energy difference (i.e., the difference in diagonal matrix elements) between the basis states coupled by the eliminated matrix element. In general, this will not be the case if we try to eliminate matrix elements between basis states with the same V (i.e., the same v quantum numbers). Also contact transformations will fail in the case of an *accidental resonance* where, for $V' \neq V$, $E^{(0)}_{V'} \approx E^{(0)}_V$.

When we diagonalize the matrix representation of the rotation-vibration Hamiltonian $\hat{H}_{\rm rv}$ we determine the eigenfunctions $\Phi_{\rm rv}^{(j)}$ of this Hamiltonian together with the eigenvalues. In the contact transformation procedure, we determine a new Hamiltonian $\tilde{H}_{\rm rv}$, whose eigenvalues are identical to those of

$\hat{H}_{\mathrm{rv}}$, but whose eigenfunctions are the basis functions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}$. The two procedures are equivalent, and from Eq. (13-111) we have

$$\Phi_{\mathrm{rv}}^{(j)} = e^{-i\hat{S}}\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}. \tag{13-120}$$

The significance of the contact transformation for the present discussion lies in the fact that when we wish to construct models for interpreting molecular rotation-vibration spectra, we will normally use a transformed Hamiltonian $\tilde{H}_{\mathrm{rv}}$ for the rotation and vibration. That is, we will start with the untransformed Hamiltonian $\hat{H}_{\mathrm{rv}}$ and then do contact transformations to remove all matrix elements with $V' \neq V$ that connect non-resonant states. The Hamiltonian resulting from these transformations, $\tilde{H}_{\mathrm{rv}}$, can be expanded in a manner similar to Eq. (13-103)

$$\tilde{H}_{\mathrm{rv}} = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} \tilde{H}_{mn}, \tag{13-121}$$

but with the important change that $\tilde{H}_{\mathrm{rv}}$ contains arbitrarily high powers n of the rotational operators, whereas $\hat{H}_{\mathrm{rv}}$ contains terms with $n \leq 2$ only. The Hamiltonian $\tilde{H}_{\mathrm{rv}}$ is totally symmetric in the MS group, just as is $\hat{H}_{\mathrm{rv}}$. Hence, when we search for perturbation terms to explain a resonance observed in an experimental spectrum, we must identify the totally symmetric terms in $\tilde{H}_{\mathrm{rv}}$ exactly as we have discussed for $\hat{H}_{\mathrm{rv}}$ above, but we are not limited to terms with $n \leq 2$. In addition to being totally symmetric in the MS group, the allowed terms in $\tilde{H}_{\mathrm{rv}}$ must be Hermitian and invariant under time reversal, so that they each contain an even number of momentum operators [$\hat{P}_r$ and $\hat{J}_\alpha$].

For example, from Eq. (13-41), in conjunction with Table 12-14, we can show by using symmetry in the MS group that in the vibrational ground state of CH$_3$F, states with $\Delta k = \pm 3$ are allowed to interact. Table 13-2 shows that this coupling can be caused by the operators

$$\left(Q_{ta}\hat{P}_{tb} - Q_{tb}\hat{P}_{ta}\right)\left[\left(\hat{J}_{\mathrm{m}}{}^{+}\right)^3 + \left(\hat{J}_{\mathrm{m}}{}^{-}\right)^3\right] \tag{13-122}$$

and

$$\left[\hat{J}_z, \left(\hat{J}_{\mathrm{m}}{}^{+}\right)^3 + \left(\hat{J}_{\mathrm{m}}{}^{-}\right)^3\right]_+, \tag{13-123}$$

where the plus commutator of two operators $\hat{A}$ and $\hat{B}$ is $[\hat{A},\hat{B}]_+ = \hat{A}\hat{B} + \hat{B}\hat{A}$. The operator in Eq. (13-122) involves normal coordinate pairs (Q_{ta}, Q_{tb}) which span the E irreducible representation of the MS group $\boldsymbol{C}_{3\mathrm{v}}(\mathrm{M})$. From Table 12-4, and from the fact that $Q_{ta}\hat{P}_{tb} - Q_{tb}\hat{P}_{ta}$ and $\hat{J}_z$ both have A_2 symmetry [Table A-6], we deduce that the operators in Eq. (13-122) and (13-123) are totally symmetric in $\boldsymbol{C}_{3\mathrm{v}}(\mathrm{M})$. They are also invariant under time reversal since they both contain four powers of momentum operators, and they are Hermitian [the operator $\hat{J}_{\mathrm{m}}{}^{+}$ is the Hermitian conjugate of $\hat{J}_{\mathrm{m}}{}^{-}$, and vice versa].

Although there are no such terms as these in $\hat{H}_{\mathrm{rv}}$, they do exist in $\tilde{H}_{\mathrm{rv}}$, and the corresponding interaction is observable in molecular spectra. In the vibrational ground state of CH_3F where all $v_t = l_t = 0$, matrix elements diagonal in the v quantum numbers vanish for the operator in Eq. (13-122), and the $\Delta k = \pm 3$ interaction will be caused solely by the operator in Eq. (13-123).

In the absence of resonances, we can use the transformed Hamiltonian $\tilde{H}_{\mathrm{rv}}$ to obtain the *effective rotational Hamiltonian*, describing the effects of centrifugal distortion and Coriolis coupling. As an example, we consider here effective rotational Hamiltonians for nonplanar asymmetric top molecules. As discussed above, for an asymmetric top the vibrational basis functions can be written as $|V\rangle = |v_1\rangle|v_2\rangle \ldots |v_{3N-6}\rangle$, where each $|v_i\rangle$ is an eigenfunction for a one-dimensional harmonic oscillator. We assume that by applying contact transformations to the rotation-vibration Hamiltonian we obtain a transformed Hamiltonian $\tilde{H}_{\mathrm{rv}}$ for which we can neglect the matrix elements off-diagonal in the v_i quantum numbers. Hence, we can average $\tilde{H}_{\mathrm{rv}}$ over one vibrational basis function $|V\rangle$ to obtain the effective rotational Hamiltonian

$$\tilde{H}_{\mathrm{rot}} = \left\langle V \left| \tilde{H}_{\mathrm{rv}} \right| V \right\rangle . \tag{13-124}$$

We refer to the Hamiltonian $\tilde{H}_{\mathrm{rot}}$ for any molecule (i.e., not only for asymmetric top molecules) as the ***Watsonian*** in recognition of the contribution made by Dr. J. K. G. Watson to its development and use [Watson (1967, 1977)]. Obviously, the Watsonian is an expansion in the rotational operators $\hat{J}_\alpha$ ($\alpha = x$, y and z) and for a nonplanar asymmetric top molecule it can be taken to have the general form [Watson (1977); see also Sarka, Papoušek, Demaison, Mäder, and Harder (1997)]

$$\begin{aligned}\tilde{H}_{\mathrm{rot}} &= B_{200}\,\hat{\boldsymbol{J}}^2 + B_{020}\,\hat{J}_z^2 + T_{400}\,\hat{\boldsymbol{J}}^4 + T_{220}\,\hat{\boldsymbol{J}}^2\,\hat{J}_z^2 + T_{040}\,\hat{J}_z^4 \\ &\quad + \frac{1}{2}\left[B_{002} + T_{202}\,\hat{\boldsymbol{J}}^2 + T_{022}\,\hat{J}_z^2, (\hat{J}_{\mathrm{m}}^+)^2 + (\hat{J}_{\mathrm{m}}^-)^2\right]_+ \\ &\quad + T_{004}\left((\hat{J}_{\mathrm{m}}^+)^4 + (\hat{J}_{\mathrm{m}}^-)^4\right),\end{aligned} \tag{13-125}$$

where we have truncated the expansion in the $\hat{J}_\alpha$ after the second order (i.e., quartic) terms. The quantities B_{ijk} and T_{ijk} in Eq. (13-125) are molecular parameters. The eigenvalues of $\tilde{H}_{\mathrm{rot}}$ are obtained by diagonalization of a Hamiltonian matrix set up in a basis of symmetric top functions $|J, k, m\rangle$ exactly as described for the Hamiltonian of the rigid asymmetric rotor in Section 11.2.4.

Experimental spectroscopic studies are aimed at determining values of the parameters B_{ijk} and T_{ijk} [and of the coefficients of higher order terms in the $\hat{J}_\alpha$ which we neglect here] by fitting differences between eigenvalues of $\tilde{H}_{\mathrm{rot}}$ to experimentally determined transition frequencies or wavenumbers. Early work showed, however, that it was impossible to determine simultaneously the values of all six T_{ijk} in Eq. (13-125) from experimental data. Watson (1967, 1977) explained this: There are infinitely many Hamiltonians $\tilde{H}_{\mathrm{rot}}$, all of the general form given in Eq. (13-125) but with different values for the T_{ijk} parameters, which have the same eigenvalues and which are equally well suited for fitting a given set of experimental data. These Hamiltonians are all connected by contact transformations. That is, if we have found one satisfactory Hamiltonian with the desired eigenvalues (i.e., a satisfactory set of B_{ijk} and T_{ijk}) we can find infinitely many other Hamiltonians with the same eigenvalues by subjecting the original one to contact transformations where the transformation operator S is an expansion in the $\hat{J}_\alpha$. Since the infinitely many Hamiltonians with common eigenvalues differ by their T_{ijk} parameter values, we cannot unambiguously determine these values from experimental data.[5] Watson (1967, 1977) elegantly solved this problem by introducing constraints on the parameters T_{ijk}. For example, for a general $\tilde{H}_{\text{rot}}$ with non-zero values for all six T_{ijk} it is possible to devise a contact transformation that produces a transformed $\tilde{H}_{\text{rot}}$ with $T_{004} = 0$. In a notation more familiar than that in Eq. (13-125), the resulting Hamiltonian is given by

$$\begin{aligned}\tilde{H}_{\text{rot}} = \frac{1}{2}(X+Y)\,\hat{\boldsymbol{J}}^2 + \left\{Z - \frac{1}{2}(X+Y)\right\}\hat{J}_z^2 - \Delta_J\,\hat{\boldsymbol{J}}^4 - \Delta_{JK}\,\hat{\boldsymbol{J}}^2\,\hat{J}_z^2 - \Delta_K\,\hat{J}_z^4 \\ + \left[\frac{1}{4}(X-Y) - \delta_J\,\hat{\boldsymbol{J}}^2 - \delta_K\,\hat{J}_z^2, (\hat{J}_{\text{m}}^{+})^2 + (\hat{J}_{\text{m}}^{-})^2\right]_+ . \qquad (13\text{-}126)\end{aligned}$$

This is known as *Watson's A-reduced Hamiltonian*. In Eq. (13-126), X, Y, and Z are the effective rotational constants of the molecule for the vibrational state in question [associated with the molecule fixed axes x, y, and z, respectively], and the parameters Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K are *centrifugal distortion constants*. The application of a contact transformation to impose selected constraints on the parameters of a Hamiltonian is called a *reduction* of the Hamiltonian. Another way of reducing the Watsonian leads to *Watson's S-reduced Hamiltonian* which has $T_{022} = 0$. We do not treat reductions in further detail here but refer the reader to the original papers by Watson (1967, 1977) and to the review article by Sarka, Papoušek, Demaison, Mäder, and Harder (1997).

For later use in Chapter 14, where we discuss details of symmetric top spectra, we summarize here some well known results regarding the energies of symmetric top molecules [see, for example, Papoušek and Aliev (1982)]. For a symmetric top, we can define the Watsonian [see Eq. (13-124)] for each vibrational state; in the absence of resonances the eigenvalues of this Hamiltonian for a prolate symmetric top can be written (in cm^{-1}) as

$$T_{VLJK} = G_{VL} + F_{VLJK} \qquad (13\text{-}127)$$

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[5] Another source of indeterminacy of the parameters is that we can use the commutator relations of the $\hat{J}_\alpha$ [Eq. (10-92)] to change the detailed form of a general expansion in these operators [Watson (1967)]. By taking $\tilde{H}_{\text{rot}}$ to be given by Eq. (13-125) we have already eliminated this source of indeterminacy here.

where

$$G_{VL} = \sum_r \omega_r \left(v_r + \frac{d_r}{2} \right) + \sum_{r \leq r'} X_{rr'} \left(v_r + \frac{d_r}{2} \right) \left(v_{r'} + \frac{d_{r'}}{2} \right) + \sum_{t \leq t'} g_{tt'} l_t l_{t'} + \ldots \tag{13-128}$$

and

$$F_{VLJK} = B_V\, J(J+1) + (A_V - B_V)\, K^2 - 2 \sum_t (A\zeta^z_{ta,tb})_V\, l_t\, k - D_J\, J^2(J+1)^2 - D_{JK}\, J(J+1)K^2 - D_K\, K^4 + \sum_t \eta^J_t\, l_t\, J(J+1)\, k + \sum_t \eta^K_t\, l_t\, k^3 + \ldots \tag{13-129}$$

with

$$B_V = B_e - \sum_r \alpha^B_r \left(v_r + \frac{d_r}{2} \right) + \ldots . \tag{13-130}$$

$$A_V = A_e - \sum_r \alpha^A_r \left(v_r + \frac{d_r}{2} \right) + \ldots . \tag{13-131}$$

$$\tag{13-132}$$

and

$$(A\zeta^z_{ta,tb})_V = A_e\, \zeta^z_{ta,tb} - \sum_r \alpha^{A\zeta_t}_r \left(v_r + \frac{d_r}{2} \right) + \ldots . \tag{13-133}$$

The expression for an oblate symmetric top is obtained by replacing A_e and A_V by C_e and C_V, respectively. As usual, in Eqs. (13-127)-(13-133) V and L are shorthand notations for all v_r and l_r quantum numbers, respectively. If ν_r is a nondegenerate normal mode, $d_r = 1$, whereas if ν_r is doubly degenerate, $d_r = 2$. We have already encountered some of the parameters in Eqs. (13-127)-(13-133). Thus ω_r in Eq. (13-128) is the quantity ω_e from Eq. (11-106) for the normal mode ν_r. The rotational constants A_e and B_e are defined in Eq. (11-9), and the Coriolis coupling constants $\zeta^z_{ta,tb}$ are defined in Eq. (10-152). However, we have introduced a number of new molecular parameters here: $X_{rr'}$, $g_{tt'}$, the centrifugal distortion constants D_J, D_{JK}, and D_K, and the constants η^J_t, η^K_t, α^B_r, α^A_r, and $\alpha^{A\zeta_t}_r$. They all depend on the equilibrium geometry [equilibrium bond lengths and angles] of the molecule and on the parameters determining the potential energy function V_N [see, for example, Papoušek and Aliev (1982)].

Generally, an effective rotational Hamiltonian commutes with the appropriate molecular rotation group and, in the absence of resonances between states coupled by the centrifugal distortion or Coriolis coupling perturbations, K is a useful near quantum number for a symmetric top. In the same way the irreducible representations of the group $\boldsymbol{D}_2$ are useful near symmetry labels for an asymmetric top. For spherical top molecules centrifugal distortion and Coriolis coupling have the important effect of causing a partial splitting of the $(2J+1)$-fold k-degeneracy of each level. The maximum splitting of this degeneracy that can occur is given by the total number of irreducible representations of the MS group that occur in Γ_{rv}. For example, the $J = 18$ level of the vibrational ground state of the methane molecule has MS group symmetry given by (see Table 12-12)

$$\Gamma_{\mathrm{rv}} = 2A_1 \oplus 2A_2 \oplus 3E \oplus 4F_1 \oplus 5F_2 \qquad (13\text{-}134)$$

and this level can be split at most into 16 components (four nondegenerate, three doubly degenerate, and nine threefold degenerate) by centrifugal distortion and Coriolis coupling. Clustering patterns in the rotational energy levels of methane when centrifugal distortion splittings are resolved were discovered by Dorney and Watson (1972), who give a simple classical explanation for them (see also Section 15.4.8). The similar clustering patterns in the centrifugally split rotational energy levels of SF_6 are discussed by Harter and Patterson (1977) and of icosahedral molecules by Harter and Weeks (1989).

If a molecule has accidental resonances, i.e., if there exists a set of two or more vibrational states $V_1, V_2, \ldots, V_n$ for which $E^{(0)}_{V_1} \approx E^{(0)}_{V_2} \approx \ldots \approx E^{(0)}_{V_n}$, contact transformations are used to eliminate the off-diagonal matrix elements coupling each of the states in the set with vibrational states V_k outside the set. Matrix elements coupling the members of the set cannot be removed by contact transformations. The contact transformation procedure leads to an effective Hamiltonian for all the states $V_1, V_2, \ldots, V_n$. For example, in Section 13.2 we discuss the interactions taking place between the three resonant vibrational states $(v_1, v_2, v_3) = (1,0,0)$, $(0,2,0)$, and $(0,0,1)$ of H_2O. It is clear that when these three states are close in energy, then the three states $(1,1,0)$, $(0,3,0)$, and $(0,1,1)$ are close in energy, the six states $(1,2,0)$, $(0,4,0)$, $(0,2,1)$ $(2,0,0)$, $(0,0,2)$, and $(1,0,1)$ are close in energy, and so on. We refer to each of these groups of vibrational states as a ***polyad***.[6] A polyad is a set of vibrational basis states that are close in energy and coupled by the anharmonic interactions important for the molecule in question. The polyads for H_2O can be characterized by the polyad quantum number [Kellman (1990)]

$$n_{\mathrm{p}} = 2v_1 + v_2 + 2v_3. \qquad (13\text{-}135)$$

The polyad consisting of $(1,0,0)$, $(0,2,0)$, and $(0,0,1)$ has $n_{\mathrm{p}} = 2$, that consisting of $(1,1,0)$, $(0,3,0)$, and $(0,1,1)$ has $n_{\mathrm{p}} = 3$, and that consisting of $(1,2,0)$, $(0,4,0)$, $(0,2,1)$ $(2,0,0)$, $(0,0,2)$, and $(1,0,1)$ has $n_{\mathrm{p}} = 4$. The terms of the Hamiltonian shown in Section 13.2 to be responsible for the interactions between the states $(1,0,0)$, $(0,2,0)$, and $(0,0,1)$ of H_2O also cause interactions within the higher polyads, but other terms can become important at higher excitation. For example, the the states $(2,0,0)$ and $(0,0,2)$ are in a Darling-Dennison resonance caused by the coupling operator $Q_1^2 Q_3^2$, and this interaction is important in polyads with $n_{\mathrm{p}} \geq 4$, but not in the lower polyads.

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[6] Polyads are sometimes called *vibrational clusters*.

Acetylene C_2H_2 is an important example of a molecule whose vibrational energy pattern has been observed to high excitation and studied in terms of polyads [see Abbouti Temsamani and Herman (1995), Herman, El Idrissi, Pisarchik, Campargue, Gaillot, Biennier, Di Lonardo, and Fusina (1998), and references therein]. The normal modes of acetylene are ν_1 (Σ_g^+), ν_2 (Σ_g^+), ν_3 (Σ_u^+), ν_4 (Π_g), and ν_5 (Π_u), where the symmetry of each normal mode in the molecular point group $\boldsymbol{D}_{\infty h}$ (see Chapter 17) is given in parentheses. The polyads are characterized by the quantum numbers [Kellman and Chen (1991), Abbouti Temsamani and Herman (1995)]

$$\begin{aligned} n_s &= v_1 + v_2 + v_3, \\ n_r &= 5v_1 + 3v_2 + 5v_3 + v_4 + v_5, \\ n_k &= l_4 + l_5, \end{aligned} \tag{13-136}$$

where the angular momentum quantum numbers l_4 and l_5 are associated with the doubly degenerate normal vibrations ν_4 and ν_5, respectively [Chapter 17].

13.2.5 The variational approach

So far we have only considered the 'standard' theory for calculating molecular rotation-vibration energies based on the harmonic oscillator-rigid rotor model described in Chapters 10 and 11. We now discuss, in an introductory fashion, more recently developed alternative approaches. Special methods for calculating the rotation-vibration energies of nonrigid molecules and weakly bound cluster molecules (see Chapter 3) are treated in Chapters 15 and 16.

The standard approach for obtaining the eigenvalues of the rotation-vibration Hamiltonian of a molecule is to use perturbation theory, normally in the form of the contact transformation procedure [see Section 13.2.4]. In this procedure, we apply contact transformations to the rotation-vibration Hamiltonian $\hat{H}_{rv}$ in order to remove all off-diagonal matrix elements connecting non-resonant states. In this manner, we obtain a matrix block describing only the rovibronic states associated with the resonant vibrational states under study, and this block can be diagonalized. Different molecules (and even different isotopomers of the same molecule) have different resonant vibrational states, and so the contact transformation procedure must be tailored for the particular isotopomer of the particular molecule under study.

In the present section we discuss approaches to molecular rotation-vibration theory that treat all interactions between basis states explicitly. We could say that they assume all vibrational states of a molecule to be resonant. They involve the construction of a truncated matrix representation of the Hamiltonian in a suitable basis set and the diagonalization of this matrix by brute computer force [see also the discussion at the beginning of Chapter 9]. As mentioned above, such an approximate procedure is called a variational calculation, and we say that the methods of the present section are examples of the *variational approach*. Perhaps it would be more correct to say the *perturbation-theory-free approach*. In a variational calculation of molecular rotation-vibration energies, it is not necessary to identify the resonant vibrational states, and consequently it is possible to develop theoretical models applicable to all molecules in a certain class [for example triatomic molecules, four-atomic acetylene-type chain molecules XYYX, pyramidal ammonia-type molecules XY_3, etc.]. This is an obvious advantage over the traditional perturbation approach. However, one disadvantage originates in the fact that in practice, many (if not most) interactions between molecular basis states are weak and could be successfully treated by perturbation theory in the form of a contact transformation. In the variational approaches, these weak interactions are treated by direct matrix diagonalization at a high cost of computer time and memory.

Whitehead and Handy (1975), following a suggestion from S. F. Boys, introduced the variational technique as a general method for calculating rotation-vibration energy levels of small molecules. They used the "standard" untransformed Hamiltonian expressed in terms of the Euler angles [i.e., molecule fixed angular momentum components] and normal coordinates; the kinetic energy operator of this Hamiltonian is given by Eq. (10-150) for a nonlinear molecule. They did not make the customary approximation of expanding the $\mu_{\alpha\beta}$ tensor elements in Eq. (10-150) as truncated power series in the normal coordinates but constructed the matrix representation of the exact Hamiltonian in a basis of products of harmonic oscillator and rigid rotor basis functions and diagonalized the resulting matrix. Calculations were carried out for H_2O, SO_2, and OCS.

Carney and Porter (1976, 1980) [see also Carney and Porter (1974)] made variational calculations to determine the vibrational energies of the H_3^+ molecular ion from an *ab initio* potential energy surface. Their Hamiltonian was expressed in terms of coordinates similar to the linearized internal coordinates S_i defined in Eq. (10-106), and they used a basis set of products of Morse oscillator eigenfunctions [see, for example, Efremov (1977) or Špirko, Jensen, Bunker, and Čejchan (1985)] and harmonic oscillator functions.

The most widespread type of variational approach employs a kinetic energy operator expressed in terms of geometrically defined vibrational coordinates and angular momentum operators. Typically, the geometrically defined vibrational coordinates are the bond lengths and bond angles ($\mathcal{R}_1$, $\mathcal{R}_2$, $\mathcal{R}_3$, ..., $\mathcal{R}_{3N-6}$) already introduced in Chapter 10 [see Eq. (10-102)]. They enter naturally into the theory when we define a parameterized, analytical function representing the potential energy function since, as discussed in Chapter 10, if the Born-Oppenheimer approximation is valid the parameters of a function expressed in terms of the $\mathcal{R}_i$ coordinates will be isotopically independent.

Many authors have obtained the kinetic energy operators for the rotation and vibration of small molecules in terms of geometrically defined vibrational coordinates [see, for example, Istomin, Stepanov, and Zhilinskii (1977), Zhilinskii, Istomin, and Stepanov (1978), and Sørensen (1979)], but the widespread use of such operators in actual calculations was heralded by Sutcliffe (1982)[7] who suggested a practical scheme for an exact transformation of the nuclear kinetic energy operator from the form depending on nuclear Cartesian coordinates [such as the (ξ_i, η_i, ζ_i)] to a form depending on three rotational coordinates, conveniently chosen as Euler angles defining the orientation in space of a *body fixed axis system* (see below), and $3N - 6$ geometrically defined vibrational coordinates $(\mathcal{R}_1, \mathcal{R}_2, \mathcal{R}_3, \ldots, \mathcal{R}_{3N-6})$. The transformation is carried out by means of the chain rule [Eq. (7-8)], i.e., it uses Method I (see Section 9.2.1).

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[7] See also Sutcliffe and Tennyson (1986) and Tennyson and Sutcliffe (1986).

The *body fixed axis system* is analogous to the molecule fixed axis system introduced in Chapter 10 in that it serves to specify the orientation of the molecule relative to the space fixed axes. However, it is not defined by use of Eckart conditions. Instead, it is rigidly attached to the *instantaneous* configuration of the molecule [so that, for example, axes can be chosen to be parallel to a bond or to bisect a bond angle in the instantaneous molecular configuration]. The origin of the body fixed axis system is usually chosen to be at the nuclear center of mass. Its orientation within the instantaneous configuration of the molecule can be chosen freely, and this choice can be used to reduce rotation-vibration interaction terms in the Hamiltonian. Sutcliffe, Tennyson and co-workers use the word "embedding" for the procedure of defining the orientation of the body fixed axis system within the instantaneous configuration of the molecule [see, for example, Tennyson (1986)].

In the 'standard' theory for molecular rotation and vibration the rotation-vibration coordinates are chosen so that certain terms in the Hamiltonian are minimized. Thus, the Eckart conditions [Chapter 10] minimize the interaction between rotation and small-amplitude vibration, and the GF calculation minimizes the coupling between individual small-amplitude vibrational modes. In the approaches based entirely on geometrically defined vibrational coordinates, little effort is made to achieve such simplifications. The vibrational coordinates are chosen in a simple way by considering the geometry of the molecule, the potential energy is chosen as a parameterized function of these coordinates, and the kinetic energy operator consistent with them is derived.

As an example of a kinetic energy operator expressed in terms of geometrically defined vibrational coordinates we quote here such an operator for a triatomic molecule ABC given by Carter and Handy (1986). These authors use the vibrational coordinates r_{AB}, r_{BC}, and α, where r_{XY} is the instantaneous value of the distance between the nuclei X and Y, and α is the instantaneous value of the bond angle $\angle(\mathrm{ABC})$. Their body fixed axis system is defined so that the y axis is the bisector of the angle $\angle(\mathrm{ABC})$. Its orientation is such that A and C have positive y coordinates. The x axis also lies in the molecular plane; it is perpendicular to the y axis and is oriented so that nucleus A is in the positive xy quadrant. The z axis completes the triad and is perpendicular to the molecular plane. With these definitions, the following expression for the kinetic energy of the rotation and vibration is obtained [see Eqs. (3.48)-(3.50) of Carter and Handy (1986)]:

$$\hat{T}_{\mathrm{N}} = \hat{T}_{\mathrm{V}} + \hat{T}_{\mathrm{VR}} \tag{13-137}$$

with

$$\begin{aligned}\hat{T}_{\mathrm{V}} = &-\frac{1}{4}\left[\left(\frac{1}{\mu_1 r_{\mathrm{AB}}^2}+\frac{1}{\mu_2 r_{\mathrm{BC}}^2}-\frac{2\cos\alpha}{m_{\mathrm{B}} r_{\mathrm{AB}} r_{\mathrm{BC}}}\right),\left(\frac{\partial^2}{\partial\alpha^2}+\cot\alpha\frac{\partial}{\partial\alpha}\right)\right]_+\\ &-\frac{1}{2\mu_1}\frac{\partial^2}{\partial r_{\mathrm{AB}}^2}-\frac{1}{2\mu_2}\frac{\partial^2}{\partial r_{\mathrm{BC}}^2}-\frac{\cos\alpha}{m_{\mathrm{B}}}\frac{\partial^2}{\partial r_{\mathrm{AB}}\partial r_{\mathrm{BC}}}\\ &+\frac{1}{m_{\mathrm{B}}}\left(\frac{1}{r_{\mathrm{AB}}}\frac{\partial}{\partial r_{\mathrm{BC}}}+\frac{1}{r_{\mathrm{BC}}}\frac{\partial}{\partial r_{\mathrm{AB}}}\right)\left(\sin\alpha\frac{\partial}{\partial\alpha}+\cos\alpha\right)\end{aligned} \tag{13-138}$$

and

$$\begin{aligned}\hat{T}_{\mathrm{VR}} = &\frac{1}{8\cos^2(\alpha/2)}\left(\frac{1}{\mu_1 r_{\mathrm{AB}}^2}+\frac{1}{\mu_2 r_{\mathrm{BC}}^2}+\frac{2}{m_{\mathrm{B}} r_{\mathrm{AB}} r_{\mathrm{BC}}}\right)\hat{\Pi}_z^2\\ &+\frac{1}{8\sin^2(\alpha/2)}\left(\frac{1}{\mu_1 r_{\mathrm{AB}}^2}+\frac{1}{\mu_2 r_{\mathrm{BC}}^2}-\frac{2}{m_{\mathrm{B}} r_{\mathrm{AB}} r_{\mathrm{BC}}}\right)\hat{\Pi}_x^2\\ &+\frac{1}{8}\left(\frac{1}{\mu_1 r_{\mathrm{AB}}^2}+\frac{1}{\mu_2 r_{\mathrm{BC}}^2}-\frac{2\cos\alpha}{m_{\mathrm{B}} r_{\mathrm{AB}} r_{\mathrm{BC}}}\right)\hat{\Pi}_y^2\\ &-\frac{1}{4\sin\alpha}\left(\frac{1}{\mu_1 r_{\mathrm{AB}}^2}-\frac{1}{\mu_2 r_{\mathrm{BC}}^2}\right)\left(\hat{\Pi}_z\hat{\Pi}_x+\hat{\Pi}_x\hat{\Pi}_z\right)\\ &-\frac{i}{2}\left(\frac{1}{\mu_1 r_{\mathrm{AB}}^2}-\frac{1}{\mu_2 r_{\mathrm{BC}}^2}\right)\left(\frac{\partial}{\partial\alpha}+\frac{\cot\alpha}{2}\right)\hat{\Pi}_y\\ &-\frac{\sin\alpha}{2m_{\mathrm{B}}}\left(\frac{1}{r_{\mathrm{BC}}}\frac{\partial}{\partial r_{\mathrm{AB}}}-\frac{1}{r_{\mathrm{AB}}}\frac{\partial}{\partial r_{\mathrm{BC}}}\right)\hat{\Pi}_y,\end{aligned} \tag{13-139}$$

where for two operators $\hat{f}$ and $\hat{g}$, $[\hat{f},\hat{g}]_+ = \hat{f}\hat{g} + \hat{g}\hat{f}$. In Eqs. (13-138)-(13-139), m_{X} (X = A, B, C) is the mass of atom X, $\mu_1 = m_{\mathrm{A}}m_{\mathrm{B}}/(m_{\mathrm{A}} + m_{\mathrm{B}})$, $\mu_2 = m_{\mathrm{C}}m_{\mathrm{B}}/(m_{\mathrm{C}} + m_{\mathrm{B}})$, and the operators $(\hat{\Pi}_x, \hat{\Pi}_y, \hat{\Pi}_z)$ are the components of the rovibronic angular momentum $\boldsymbol{J}$ about the body fixed axes (x, y, z); these components are defined with a sign convention [see Eq. (3.31) of Carter and Handy (1986)] that makes them obey the 'space-fixed' commutation relations of Eq. (10-90) with J replaced by Π. Additional examples of kinetic energy operators for triatomic molecules derived in terms of different types of geometrically defined coordinates are given by Handy (1987) and by Sutcliffe and Tennyson (1991).

The kinetic energy operator in Eqs. (13-138)-(13-139) should be compared to the 'standard' kinetic energy operator for rotation and vibration given in Eqs. (10-150)-(10-154). In the standard operator of Eq. (10-150), we replace the $\mu_{\alpha\beta}$ functions by Taylor expansions, truncated at a finite order, in the normal coordinates [see Eq. (10-154)]. No analogous approximation is made in the closed-form kinetic energy operator of Eqs. (13-138)-(13-139). This operator is exactly equal to (so that it has the same eigenvalues as) the original rotation-vibration Hamiltonian expressed in Cartesian nuclear coordinates (ξ_i, η_i, ζ_i). The relatively simple form of the operator $\hat{T}_{\mathrm{N}}$ in Eq. (13-137) is due to the simple relationships between the geometrically defined coordinates $(r_{\mathrm{AB}}, r_{\mathrm{BC}}, \alpha)$

and the Cartesian coordinates of the nuclei in the body fixed axis system. These relationships are simple because the body fixed axis system is rigidly attached within the instantaneous nuclear geometry of the molecule. In the standard theory, the corresponding relationships between the geometrically defined coordinates and the Cartesian coordinates of the nuclei in the molecule fixed axis system are much more complicated because the molecule fixed axis system is defined by using the Eckart conditions [see Section 10.2.1]. The mathematical simplicity of the kinetic energy operator, and the fact that it can be obtained from the Cartesian-coordinate dependent operator without approximation, are obvious advantages of the approach described here. The most important disadvantage is that in the T_N of Eq. (13-137), rotation-vibration interaction is not minimized since the Eckart equations are not satisfied by the nuclei coordinates in the body fixed axis system. In order to make an accurate variational calculation of the eigenvalues of the rotation-vibrational Hamiltonian obtained from T_N, it is necessary to use basis sets much larger than those necessary for diagonalizing the 'standard' Hamiltonian, particularly for the calculation of highly excited rotational states. Consequently, at present the variational approach involving geometrically defined vibrational coordinates is limited to small molecules. Recently, however, Wei and Carrington (1997) have used the Eckart conditions in a derivation of the exact kinetic energy operator for a triatomic molecule in terms of the instantaneous bond lengths and included angle.

The eigenvalues of the rotation-vibration Hamiltonian obtained by adding a kinetic energy operator such as T_N of Eq. (13-137) to the Born-Oppenheimer potential energy function V_N [which is represented by a parameterized analytical function of the geometrically defined vibrational coordinates] are typically calculated by diagonalizing the matrix representation of the Hamiltonian in a truncated, suitably chosen set of basis functions, i.e., in a standard variational calculation as described by Eqs. (6-144)-(6-162). In such a calculation, the initially unknown wavefunction is expressed as a linear combination of known basis functions [Eq. (6-148)]. In practical calculations, a finite number, N_B say, of basis functions is used and it is sometimes said that the wavefunction is obtained in a *Finite Basis Representation (FBR)*. Wavefunctions expressed in an FBR are determined by solving the N_B ***coupled equations*** given by Eq. (6-158) or (6-159). A successful alternative to using an FBR for representing the wavefunction is to use a DVR [a ***Discrete Variable Representation***; see Lill, Parker, and Light (1982), and Light, Hamilton, and Lill (1985)]. The DVR is obtained by subjecting the N_B coupled equations of Eq. (6-158) to a unitary transformation producing another set of N_B coupled equations. Whereas in the original (FBR) system of coupled equations, we have one equation for each basis function in the chosen basis set [e.g., the equations given by Eq. (6-158) are labeled by the index m numbering the basis functions], each DVR equation is associated with (and thus labeled by) a quadrature point [i.e., a particular value] of the appropriate geometrically defined vibrational coordinates. The fact that we obtain equations associated with particular values of the coordinates is referred to as a ***discretization*** of the coordinates. The pointwise DVR representation of the wavefunction on N_B quadrature points is equivalent to the FBR representation in a set of N_B basis functions and as already mentioned, the two representations are related by an unitary transformation. By judiciously choosing the analytical function used to represent the potential energy function, one can achieve in the DVR approach a situation in which the matrix of the potential energy function is diagonal in the quadrature points.

For example, if we consider again the triatomic molecule with vibrational coordinates r_{AB}, r_{BC}, and α, we can choose to treat the bending vibration, described by α, in a DVR. We obtain N_B DVR equations, each equation being labeled by α_k ($k = 1, 2, 3, \ldots, N_B$), a particular value of α. A major advantage offered by the DVR approach is that we can initially treat the remaining (stretching) vibrations, described by r_{AB} and r_{BC}, separately at each of the N_B discrete α-values α_k. The stretching vibrational wavefunctions obtained at the individual α_k values will form a highly optimized basis for treating the complete vibrational problem, and accurate results can be obtained also when relatively few such functions are used as basis functions for the final problem. That is, the DVR approach provides a natural way of splitting the large calculation of the rotation-vibration eigenvalues into many smaller calculations.

Bačić and Light (1986, 1987, 1989) have carried out vibrational calculations at discrete coordinate values by using a *Distributed Gaussian basis (DGB).* In our example of the triatomic molecule with vibrational coordinates r_{AB}, r_{BC}, and α, we need to solve the stretching vibrational problem at a number of fixed α-values α_k. In the *DVR-DGB* method of Bačić and Light (1986, 1987, 1989), this would be done by expanding the stretching wavefunctions in basis functions such as

$$\phi_i^{(k)}(r_{AB}, r_{BC}) = \sqrt{\frac{2A_i^{(k)}}{\pi}} \exp\left\{-A_i^{(k)}\left[(r_{AB} - r_{AB,i}^{(k)})^2 + (r_{BC} - r_{BC,i}^{(k)})^2\right]\right\}. \tag{13-140}$$

where the parameters $A_i^{(k)}$, and the number of $\phi_i^{(k)}$ functions used to represent a stretching wavefunction, can be allowed to vary from one angle α_k to another. The functions in Eq. (13-140) are the "Gaussian nipples" mentioned at the beginning of Chapter 9.

In all the theoretical methods treated in the present section, the initially unknown rotation-vibration wavefunctions are expressed as linear combinations of known basis functions. We have not discussed the detailed form of the basis functions, but obviously they can be symmetrized in the MS group and in **K**(spatial) in exactly the same manner as harmonic oscillator and rigid rotor basis functions can be symmetrized. Thus, the MS group and **K**(spatial) symmetry can be used to facilitate variational calculations. We refer the reader to the original literature for detailed discussions of such applications of symmetry. For example, Špirko, Jensen, Bunker, and Čejchan (1985) discuss in detail how Morse oscillator eigenfunctions, used as vibrational basis functions for H_3^+, are symmetrized in $\boldsymbol{D}_{3h}(M)$.

13.2.6 The vibron model

The vibron model, or algebraic method, is a recently developed alternative for describing and analyzing rotation-vibration energy levels and spectra [Iachello (1981), Iachello and Levine (1995)]. In this model the two (one raising and one lowering) Morse oscillator ladder operators for each bond in the molecule are used, and they are said to form an *algebra* that describes the stretching energy levels of the bond. Interactions between the bonds are introduced by coupling the individual bond algebras in a manner akin to that used in coupling angular momenta. The coupled algebra can be reduced to one or more chains of sub-algebras, defining the so-called *dynamical symmetry* of the system. The eigenvalues of the invariant (or Casimir) operators of each member of the chain, i.e., operators that commute with every operator in a given algebra,[8] yield a closed expression for the vibrational energy of the molecule in the local mode limit. Transformation to the normal mode picture introduces a *Majorana operator* [van Roosmalen, Iachello, Levine and Dieperink (1983), van Roosmalen, Benjamin and Levine (1984)] that contributes both diagonal and off-diagonal terms to the energy matrix. Diagonalization of the resulting block-diagonal matrix yields the vibrational energy levels of the molecule.

This model has a certain simplicity that makes it appealing, but in its simple form it generally lacks sufficient accuracy for fitting spectroscopic data. We will use the water molecule as an example and label the two bonds 1 and 3. Each bond contributes a term of the form $E_0 - 4A(Nv - v^2)$, where the parameters A and N are given in terms of the constants of the Morse potential $D\{1 - \exp[-\beta(r - r_e)]\}^2$ by $A = -\hbar^2\beta^2/(8\mu)$ and $N = 2(2\mu D)^{1/2}/(\hbar\beta)$; μ is the reduced mass of the atoms forming the bond, v is the vibrational quantum number, and E_0 is a constant. N is called the *vibron number* and it is equal to twice the number of bound states of the Morse oscillator. The pairing of the bonds adds the term $-4A_{13}[(N_1 + N_3)(v_1 + v_3) - (v_1 + v_3)^2]$. Thus the exact local mode formula for the vibrational energy of the H_2O molecule involves just three parameters $N_1 = N_3$, $A_1 = A_3$, and A_{13}. Transition to the normal mode representation adds to the energy expression one more parameter, λ, which multiplies the matrix elements of the Majorana operator connecting states within each block having the same value of the quantum number sum $(v_1 + v_{\text{bend}} + v_3)$.

The lack of accuracy, particularly for reproducing the values of bending energy levels, can be partially corrected by adding higher order terms (as in a Dunham expansion). But this then makes the energy formula more complicated. Extensions are needed in order to include rotations and large amplitude vibrations, and for the calculation of vibronic and rovibronic intensities. New ideas like this (it still seems to be the case for the molecular symmetry group more than 30 years after its introduction) do seem to take an extraordinary long time to merge into the mainstream. Clearly, well publicized solutions to interesting problems using the vibron model are necessary (but unfortunately not sufficient) to make this merging occur. The four references quoted in this short section could form a basis for further study of this approach.

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[8] An easily appreciated example of a Casimir operator is the total angular momentum operator $\hat{J}^2$ which commutes with $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$.

13.3 VIBRONIC AND ROVIBRONIC INTERACTIONS

Interactions between the rovibronic levels of one electronic state and the rovibronic levels of another electronic state are caused by one of the following kinetic energy terms in the molecular Hamiltonian:[9]

$$\hat{T}_{\rm vib} = \frac{1}{2}\sum_{r} \hat{P}_r{}^2, \tag{13-141}$$

$$\hat{T}_{\rm ev} = \frac{1}{2}\sum_{\alpha,\beta} \mu_{\alpha\beta}(\hat{p}_\alpha \hat{L}_\beta + \hat{L}_\alpha \hat{p}_\beta), \tag{13-142}$$

$$\hat{T}_{\rm er} = -\frac{1}{2}\sum_{\alpha,\beta} \mu_{\alpha\beta}(\hat{J}_\alpha \hat{L}_\beta + \hat{L}_\alpha \hat{J}_\beta), \tag{13-143}$$

and

$$\hat{T}_{\rm ee} = \frac{1}{2}\sum_{\alpha,\beta} \mu_{\alpha\beta}\hat{L}_\alpha \hat{L}_\beta. \tag{13-144}$$

See Eq. (10-144) for $\hat{T}_{\rm vib}$ and Eq. (10-150) for $\hat{T}_{\rm er} + \hat{T}_{\rm ev} + \hat{T}_{\rm ee}$. In these expressions the normal coordinates are taken to be those of one of the electronic states, $\Phi_{\rm elec}^{(e,S,m_S)}$ say, and the normal coordinates of the other electronic state, $\Phi_{\rm elec}^{(e',S',m_S')}$ say, are expressed in terms of them. Similarly the elements of $\mu_{\alpha\beta}$ are expanded about the equilibrium configuration of the state $\Phi_{\rm elec}^{(e,S,m_S)}$ in the normal coordinates of that state. Without making further approximations all we can say is that [in Hund's case (b)] these terms couple states that have the same N ($= J$ for singlet states), I and S quantum numbers, and the same MS group species $\Gamma_{\rm rve}$; the term $\hat{T}_{\rm vib}$ will mix states having the same $\Gamma_{\rm rot}$ and $\Gamma_{\rm ve}$. The MS group is now that appropriate for the simultaneous treatment of the electronic states under consideration. Apart from two special cases involving electronic degeneracy (to be discussed below), and in Rydberg states, the dominant interactions can be determined by making some appropriate approximations and by using near symmetry and near quantum numbers. Vibronic and rovibronic interactions cause the breakdown of the Born-Oppenheimer approximation since they involve the coupling of different electronic states.

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[9] In Hund's case (a) there will also be terms involving products such as $\hat{J}_\alpha \hat{S}_\beta$, $\hat{p}_\alpha \hat{S}_\beta$, and $\hat{L}_\alpha \hat{S}_\beta$; see footnote on page 299.

Interactions between the energy levels of two electronic states are clearly going to be most important if the electronic states involved are close in energy with respect to the rotation-vibration energy level spacing. However, in an isolated electronic ground state the cumulative effect of interaction with all possible electronic excited states gives rise to small corrections to the rotation-vibration energies. Such corrections are most apparent when one compares the ground electronic state rotation-vibration energies of isotopomers. A perturbation theory approach is clearly appropriate, and Bunker and Moss (1977) show how the standard contact transformation procedure discussed in Section 13.2.4 can be applied here. The standard contact transformation procedure is used above to eliminate matrix elements between the vibrational state under study and other vibrational states within a single electronic state. This leads to the development of an effective rotational Hamiltonian (the Watsonian) for that vibrational state. In the work of Bunker and Moss (1977) it is shown how the contact transformation method can be used to eliminate matrix elements between the ground electronic state and excited electronic states to give an effective rotation-vibration Hamiltonian for the ground electronic state. The theory requires that allowance be made in the contact transformation for the fact that the zero order electronic energies are not constants but are dependent on the nuclear geometry. The effective rotation-vibration Hamiltonian [developed for diatomic molecules in Bunker and Moss (1977) and for triatomic molecules in Bunker and Moss (1980)] contains nuclear mass dependent correction terms that account for the effect of the interactions with excited electronic states. Bunker, McLarnon and Moss (1977) have applied the theory to the electronic ground state of H_2 and D_2.

Watson (1980) has shown how the eigenvalues of the effective rotation-vibration Hamiltonian of a diatomic molecule can be cast in a way that explicitly gives their isotopic dependence. It is shown that if we use v as the harmonic oscillator quantum number and J as the angular momentum quantum number the eigenvalues E_{vJ} of the effective rotation-vibration Hamiltonian of an isolated singlet electronic ground state can be written as the standard ***Dunham expansion*** [Dunham (1932)]

$$E_{vJ} = hc\sum_{k=0}^{\infty}\sum_{l=0}^{\infty} Y_{kl}\left(v+\frac{1}{2}\right)^{k}\left[J(J+1)-\Lambda^2\right]^{l}, \tag{13-145}$$

where Λ is the projection of the electronic angular momentum on the molecular axis in units of $\hbar$. Allowing for the breakdown of the Born-Oppenheimer approximation to second order the Dunham coefficients are given by

$$Y_{kl} = \mu_C^{(k+2l)/2}\, U_{kl}\left\{1 + m_e\Delta_{kl}^{a}/M_a + m_e\Delta_{kl}^{b}/M_b + \mathrm{O}(m_e^2/M_i^2)\right\}, \tag{13-146}$$

where m_e is the electron mass, M_a and M_b are the two atomic masses, and μ_C is the charge-modified reduced mass

$$\mu_C = M_a\, M_b/(M_a + M_b - C\, m_e), \tag{13-147}$$

where C is the charge number of the molecule, so that the denominator in μ_C is the total mass. An important result of Watson (1980) is that the U_{kl} and the Δ^i_{kl} are nuclear mass independent constants. The correction represented by $O(m_e^2/M_i^2)$ in Eq. (13-146) is usually too small to characterize experimentally. One can substitute Eq. (13-146) into Eq. (13-145) to obtain an equation that can be used in the fitting of rotation-vibration energy level data for all isotopomers of a diatomic molecule simultaneously, and the outcome will be values for the constants U_{kl} and Δ^i_{kl}. In making such a fitting one must be aware of the constraints among the U_{kl}.[10] Such a fitting has been performed for the isotopomers of CO by Farrenq, Guelachvili, Sauval, Grevesse and Farmer (1991).

It can happen that two electronic states become degenerate for a particular (symmetrical) nuclear arrangement, and in this circumstance the interactions become all pervasive; our zero order separable wavefunction becomes a very poor approximation. This happens in the Renner effect [Renner (1934)] and in the Jahn-Teller effect [Jahn and Teller (1937)]. Electronic degeneracy, or near degeneracy, also occurs in a systematic way in electronic Rydberg states. These three cases are treated separately below. When the two electronic states involved are not close in energy (compared to vibrational energy separations) we can appreciate the dominant effects by considering that the two electronic states involved have the same equilibrium nuclear geometry and harmonic force constants (i.e., identical normal coordinates), and that the dependence of the $\mu_{\alpha\beta}$ elements occurring in Eqs. (13-142)-(13-144) on the normal coordinates can be neglected [see Eq. (10-154)].

13.3.1 The effect of $\hat{T}_{\text{vib}}$

Making the approximations just mentioned above we can write the matrix element for the *vibronic* interaction caused by $\hat{T}_{\text{vib}}$ between the states

$$\Phi^0_{\text{int}} = \Phi_{\text{nspin}}\Phi_{\text{rot}}\Phi_{\text{vib}}\Phi^{(e,S,m_S)}_{\text{elec}} \tag{13-148}$$

and

$$\Phi^{0'}_{\text{int}} = \Phi_{\text{nspin}}\Phi_{\text{rot}}\Phi'_{\text{vib}}\Phi^{(e',S,m_S)}_{\text{elec}} \tag{13-149}$$

as the sum of the following two terms:

$$\begin{aligned} H_1 &= \left\langle \Phi_{\text{vib}} \left| \sum_r \left\langle \Phi^{(e,S,m_S)}_{\text{elec}} \left| \hat{P}_r \right| \Phi^{(e',S,m_S)}_{\text{elec}} \right\rangle \hat{P}_r \right| \Phi'_{\text{vib}} \right\rangle \\ &= \left\langle \Phi_{\text{vib}} \left| \sum_r X_r^{ee'} \hat{P}_r \right| \Phi'_{\text{vib}} \right\rangle, \end{aligned} \tag{13-150}$$

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[10] **See Eq. (10) of Tyuterev and Velichko (1984). Three misprints in these constraints are corrected in the Appendix of Farrenq, Guelachvili, Sauval, Grevesse and Farmer (1991); note that in this Appendix the paper referred to as Ref. (31) should be called Ref. (32).**

where

$$X_r^{ee'} = \left\langle \Phi_{\mathrm{elec}}^{(e,S,m_S)} \middle| \hat{P}_r \middle| \Phi_{\mathrm{elec}}^{(e',S,m_S)} \right\rangle, \tag{13-151}$$

and

$$\begin{aligned} H_2 &= \left\langle \Phi_{\mathrm{vib}} \middle| \left\langle \Phi_{\mathrm{elec}}^{(e,S,m_S)} \middle| \frac{1}{2}\sum_r \hat{P}_r{}^2 \middle| \Phi_{\mathrm{elec}}^{(e',S,m_S)} \right\rangle \middle| \Phi'_{\mathrm{vib}} \right\rangle \\ &= \langle \Phi_{\mathrm{vib}} | Y^{ee'} | \Phi'_{\mathrm{vib}} \rangle, \end{aligned} \tag{13-152}$$

where

$$Y^{ee'} = \left\langle \Phi_{\mathrm{elec}}^{(e,S,m_S)} \middle| \frac{1}{2}\sum_r \hat{P}_r{}^2 \middle| \Phi_{\mathrm{elec}}^{(e',S,m_S)} \right\rangle. \tag{13-153}$$

The two interacting states must have the same rotational and nuclear spin wavefunctions, the same S values, and the same m_S values since T_{vib} does not involve the coordinates associated with rotation, nuclear spin, and electron spin. In making the Born-Oppenheimer approximation (see Chapter 9) we neglect the effect of the operators $\hat{P}_r$ on the electronic wavefunctions $\Phi_{\mathrm{elec}}^{(e,S,m_S)}$, i.e., we set $\hat{P}_r\Phi_{\mathrm{elec}}^{(e,S,m_S)} = 0$. Consequently the terms in Eqs. (13-150) and (13-152) correct for some of the inaccuracy introduced by the Born-Oppenheimer approximation. For $\Phi_{\mathrm{elec}}^{(e,S,m_S)} = \Phi_{\mathrm{elec}}^{(e',S,m_S)}$, i.e., for $e' = e$, we refer to these matrix elements as *adiabatic correction terms*; for $\Phi_{\mathrm{elec}}^{(e,S,m_S)} \neq \Phi_{\mathrm{elec}}^{(e',S,m_S)}$ they are *nonadiabatic correction terms*. The term H_1 is much larger than H_2 since it is the matrix element of a function involving the vibrational momenta whereas H_2 is the matrix element of a function of vibrational coordinates; we normally neglect H_2.

If, in H_1, we neglect the dependence of $X_r^{ee'}$ on the normal coordinates (i.e., consider only the first term, $X_{r0}^{ee'}$, say, in the Taylor series expansion of $X_r^{ee'}$ about the equilibrium nuclear configuration) then it is totally symmetric in the MS group, and we must have

$$\Gamma_{\mathrm{elec}} \otimes \Gamma(\hat{P}_r) \otimes \Gamma'_{\mathrm{elec}} \supset \Gamma^{(s)}. \tag{13-154}$$

Equivalently,

$$\Gamma_{\mathrm{elec}} \otimes \Gamma'_{\mathrm{elec}} \supset \Gamma(Q_r). \tag{13-155}$$

With $X_{r0}^{ee'}$ not depending on the normal coordinates we can write

$$H_1 = \sum_r X_{r0}^{ee'} \langle \Phi_{\mathrm{vib}} | \hat{P}_r | \Phi'_{\mathrm{vib}} \rangle \tag{13-156}$$

and for the matrix element of $\hat{P}_r$ to be nonvanishing we must have

$$\Delta v_r = \pm 1 \tag{13-157}$$

in the harmonic oscillator approximation (see Table 11-2).

The dominant vibronic interaction from $\hat{T}_{\mathrm{vib}}$ will therefore be between vibronic states for which the electronic states have symmetry connected by that of a normal coordinate, and the vibrational states have vibrational quantum numbers that differ by one for a vibration whose normal coordinate has the species to connect the two electronic states. In the SCF approximation for the electronic states we have further restrictions on the changes in the MO occupation number n_i. The operator $\hat{P}_r$ is a one-electron operator [Brillouin (1934)] and its matrix elements will vanish if the electron configurations of the states differ by more than one orbital [see Sidis and Lefebvre-Brion (1971)]. For example, the configurations of the $\tilde{X}\,^2A_1$ and $\tilde{B}\,^2B_2$ states of NO_2 [MS group $\boldsymbol{C}_{2v}(\mathrm{M})$; see Table A-5] are

$$\tilde{X}\,^2A_1: \quad \cdots(1\mathrm{a}_2)^2(4\mathrm{b}_2)^2(6\mathrm{a}_1)^1 \tag{13-158}$$

and

$$\tilde{B}\,^2B_2: \quad \cdots(1\mathrm{a}_2)^2(4\mathrm{b}_2)^1(6\mathrm{a}_1)^2, \tag{13-159}$$

which differ by one orbital for one electron and have species that are connected by that of a normal coordinate [the three normal coordinates of NO_2 have symmetries $\Gamma(Q_1) = \Gamma(Q_2) = A_1$ and $\Gamma(Q_3) = B_2$]. Hence there will be a non-zero vibronic interaction matrix element satisfying $\Delta v_3 = \pm 1$ between vibrational levels of these states from the term H_1.

13.3.2 The effect of $\hat{T}_{\mathrm{ev}}$

The term $\hat{T}_{\mathrm{ev}}$, like $\hat{T}_{\mathrm{vib}}$, causes vibronic interactions and it will couple states, such as those represented in Eqs. (13-148) and (13-149), that differ in vibrational and electronic state only. Neglecting the dependence of $\mu_{\alpha\beta}$ and of the matrix elements of $\hat{L}_\alpha$ on the normal coordinates the dominant matrix element is

$$\sum_\alpha \mu^{\mathrm{e}}_{\alpha\alpha}\left[\left\langle \Phi_{\mathrm{elec}}^{(\epsilon,S,m_S)}\middle|\hat{L}_\alpha\middle|\Phi_{\mathrm{elec}}^{(\epsilon',S,m_S)}\right\rangle\left\langle\Phi_{\mathrm{vib}}\middle|\hat{p}_\alpha\middle|\Phi'_{\mathrm{vib}}\right\rangle\right]. \tag{13-160}$$

The operators $\hat{p}_\alpha$ and $\hat{L}_\alpha$ transform like $\hat{J}_\alpha$ so that the symmetry conditions for this matrix element to be nonvanishing are

$$\Gamma_{\mathrm{elec}} \otimes \Gamma'_{\mathrm{elec}} \supset \Gamma(\hat{J}_\alpha) \tag{13-161}$$

and

$$\Gamma_{\mathrm{vib}} \otimes \Gamma'_{\mathrm{vib}} \supset \Gamma(\hat{J}_\alpha), \tag{13-162}$$

where $\alpha = x, y$, or z. Assuming the same harmonic force field for the two electronic states, and using Eq. (10-151) for p_α we deduce the vibrational selection rules to be

$$\Delta v_r = \pm 1, \qquad \Delta v_s = \pm 1,$$

where

$$\Gamma(Q_r) \otimes \Gamma(Q_s) \supset \Gamma(J_\alpha). \tag{13-163}$$

13.3.3 The effect of $\hat{T}_{\rm er}$

With the exception of the Renner effect (see below), the dominant effect in a rigid molecule of the rotational kinetic energy coupling term $\hat{T}_{\rm er}$ [see Eq. (13-143)] is understood if we neglect the dependence of $\mu_{\alpha\beta}$, and of the matrix elements of $\hat{L}_\alpha$, on the normal coordinates. In this circumstance $\hat{T}_{\rm er}$ only involves the rotational and electronic coordinates so that $\Phi_{\rm nspin}$ and $\Phi_{\rm vib}$ (as well as the basis symmetry label $\Gamma_{\rm re} = \Gamma_{\rm rot} \otimes \Gamma_{\rm elec}$) must be the same for the states that are coupled. Also, the interacting states must have the same values of S and m_S. The dominant interaction is a *rotation-electronic* interaction and the relevant matrix element of $\hat{T}_{\rm er}$ is

$$-\sum_\alpha \mu^e_{\alpha\alpha}\left[\left\langle \Phi^{(e,S,m_S)}_{\rm elec}\middle|\hat{L}_\alpha\middle|\Phi^{(e',S,m_S)}_{\rm elec}\right\rangle \left\langle \Phi_{\rm rot}\middle|\hat{J}_\alpha\middle|\Phi'_{\rm rot}\right\rangle\right], \tag{13-164}$$

where $\alpha = x, y$, or z. For the matrix element of $\hat{L}_\alpha$ between the electronic wavefunctions to be nonvanishing the electronic species must be connected by a rotation (since $\hat{L}_\alpha$ transforms like $\hat{J}_\alpha$), i.e.,

$$\Gamma_{\rm elec} \otimes \Gamma'_{\rm elec} \supset \Gamma(\hat{L}_\alpha) = \Gamma(\hat{J}_\alpha), \tag{13-165}$$

where $\alpha = x, y$, or z. The rotational selection rules will depend on which of the three rotations is involved in Eq. (13-165).

For a symmetric top molecule if the product of the electronic species is that of $\hat{J}_z$ then the electronic matrix element of $\hat{L}_z$ can be nonvanishing and the allowed interaction must have $\langle\Phi_{\rm rot}|\hat{J}_z|\Phi'_{\rm rot}\rangle \neq 0$. If Eq. (13-165) involves the x and y components for a symmetric top then the rotational states coupled must be such that $\langle\Phi_{\rm rot}|\hat{J}_x|\Phi'_{\rm rot}\rangle$ or $\langle\Phi_{\rm rot}|\hat{J}_y|\Phi'_{\rm rot}\rangle \neq 0$. In the molecular rotation group $\boldsymbol{D}_\infty$ the angular momenta $(\hat{J}_x, \hat{J}_y)$ transform as Π, and $\hat{J}_z$ as Σ^- (see Table 12-15). As a result, by classifying the rigid rotor functions $\Phi_{\rm rot}$ and $\Phi'_{\rm rot}$ in $\boldsymbol{D}_\infty$ we see that, from the vanishing integral rule [Eq. (6-140)],

$$\langle\Phi_{\rm rot}|\hat{J}_z|\Phi'_{\rm rot}\rangle \neq 0 \tag{13-166}$$

implies that in $\boldsymbol{D}_\infty$

$$\Gamma(\Phi_{\rm rot}) \otimes \Sigma^- \otimes \Gamma(\Phi'_{\rm rot}) \supset \Sigma^+$$

i.e.,

$$\Gamma(\Phi_{\rm rot}) \otimes \Gamma(\Phi'_{\rm rot}) \supset \Sigma^-$$

or [see Herzberg (1991b), p. 572]

$$K = K' \tag{13-167}$$

(with $K > 0$ since $J = J'$). Similarly

$$\langle \Phi_{\rm rot} | \hat{J}_x | \Phi'_{\rm rot} \rangle \neq 0 \text{ or } \langle \Phi_{\rm rot} | \hat{J}_y | \Phi'_{\rm rot} \rangle \neq 0 \tag{13-168}$$

implies [see Herzberg (1991b), p. 572]

$$K = K' \pm 1. \tag{13-169}$$

Thus for a symmetric top molecule the dominant interactions caused by $\hat{T}_{\rm er}$ will be between electronic states having symmetry connected by a rotation, and rotational states coupled have the selection rule $\Delta K = 0$ or ± 1 depending on which rotational symmetry couples the electronic states. Centrifugal distortion or Coriolis coupling mixes states of different K within the same electronic state [see Eqs. (13-76) and (13-79)] and spoils the usefulness of the selection rules on K.

For an asymmetric top molecule using the $\boldsymbol{D}_2$ molecular rotation group (see Table 12-16) we see that the rotational selection rules will be ($\Delta K_a =$ even, $\Delta K_c =$ odd), ($\Delta K_a =$ odd, $\Delta K_c =$ odd), and ($\Delta K_a =$ odd, $\Delta K_c =$ even) as the product of the species of the electronic states is that of $\hat{J}_a$, $\hat{J}_b$, and $\hat{J}_c$, respectively. If for the states concerned the molecule is a near prolate rotor (i.e., K_a is a useful near quantum number) then $\Delta K_a =$ even (or odd) can be replaced by $\Delta K_a = 0$ (or ± 1); for a near oblate rotor similar remarks apply for ΔK_c.

13.3.4 The effect of $\hat{T}_{\rm ee}$

If, once again, we assume $\mu_{\alpha\beta}$ and the matrix elements of $\hat{L}_\alpha$ to be independent of the normal coordinates (which, as we see below, we cannot do in the Renner effect), then we obtain the dominant matrix element of $\hat{T}_{\rm ee}$ as

$$P^{ee'} = \sum_\alpha \mu^e_{\alpha\alpha} \left[\left\langle \Phi^{(e,S,m_S)}_{\rm elec} \middle| \hat{L}^2_\alpha \middle| \Phi^{(e',S,m_S)}_{\rm elec} \right\rangle \right]. \tag{13-170}$$

In order that $\hat{T}_{\rm ee}$ [Eq. (13-144)] can be totally symmetric in the MS group in the approximation of $\mu_{\alpha\alpha}$ being constant and equal to $\mu^e_{\alpha\alpha}$, $\hat{L}^2_\alpha$ must be totally symmetric. Thus the matrix element of Eq. (13-170) will vanish unless

$$\Gamma_{\rm elec} = \Gamma'_{\rm elec}. \tag{13-171}$$

This means that $\hat{T}_{ee}$ has nonvanishing matrix elements diagonal in the electronic state, i.e., with $\Phi_{\text{elec}}^{(e,S,m_S)} = \Phi_{\text{elec}}^{(e',S,m_S)}$. These matrix elements are adiabatic correction terms.

The full adiabatic correction to the Born-Oppenheimer potential energy surface is given by

$$\Delta V_{\text{ad}} = P^{ee} + Y^{ee} + \langle\Phi_{\text{elec}}^{(e,S,m_S)}|\hat{T}'_{\text{e}}|\Phi_{\text{elec}}^{(e,S,m_S)}\rangle, \tag{13-172}$$

where Y_r^{ee} comes from Eq. (13-153) and $\hat{T}'_{\text{e}}$ from Eq. (9-49). All these terms are nuclear mass dependent. Adding this to the Born-Oppenheimer potential gives the adiabatic potential energy surface.

13.4 THE RENNER EFFECT AND THE JAHN-TELLER EFFECT

At certain symmetrical nuclear configurations in a molecule the point group is such that there are degenerate irreducible representations in the group. Thus there can be degenerate electronic states at that nuclear configuration. When the nuclei move from this symmetrical arrangement to a less symmetrical one the degeneracy can be resolved and the electronic degeneracy of the potential energy surface at the symmetrical nuclear configuration split. In the Renner effect the symmetrical nuclear arrangement is that in which the molecule is linear, and in which therefore the electronic states can be doubly degenerate of Π, Δ, Φ, ... symmetry in the $\boldsymbol{C}_{\infty\text{v}}$ or $\boldsymbol{D}_{\infty\text{h}}$ point group as appropriate. On bending the degeneracy will be lifted, and the splitting has to be a symmetric (even) function of ρ, the angle of deviation from linearity; in lowest order it would be a quadratic function of ρ. Thus in the Renner effect the two potential energy surfaces that meet at linear geometries of the molecule could both have their minima at the linear geometry. The Jahn-Teller effect occurs when a pair of electronic states of a polyatomic molecule are degenerate at a particular symmetrical nonlinear nuclear configuration. Such electronic states will always have their energy split by some nuclear distortion. It can be shown [Jahn and Teller (1937)] that in first order, the splittings are linear in the nuclear coordinates. This means that the minimum will not be at the symmetrical nuclear configuration for one of the electronic states. In these circumstances it is ironic that to deal with the symmetry of the rovibronic states one uses the MS group that is isomorphic to the point group of the bent molecule in the Renner effect (even though the minimum energy structure may well be linear), and one uses the MS group isomorphic with the point group of the symmetrical structure in the Jahn-Teller effect (even though the minimum is never at that geometry). The Jahn-Teller effect is predominantly a *vibronic* interaction between electronic states, whereas the Renner effect is a *rovibronic* interaction.

13.4.1 The Renner effect

Usually electronic matrix elements of $\hat{L}_\alpha$ are smaller than those of $\hat{P}_r$ so that $\hat{T}_{\text{vib}}$ is the dominant cause of the breakdown of the Born-Oppenheimer approximation. However, there is one case where interactions by $\hat{T}_{\text{er}}$ and $\hat{T}_{\text{ee}}$ can be very important, and that is for 'chain' molecules such as HC_4H^+, HC_3N (cyano-acetylene), HCCH, NH_2 or HCN, that can easily vibrate through a linear configuration in one or more electronic states. In this circumstance the coefficient μ_{zz} (where z is the axis of linearity) in Eqs. (13-143) and (13-144) becomes very large in the region of the linear configuration, and also it turns out that electronic states coupled by $\hat{T}_{\text{er}}$ can be very close in energy for such molecules.

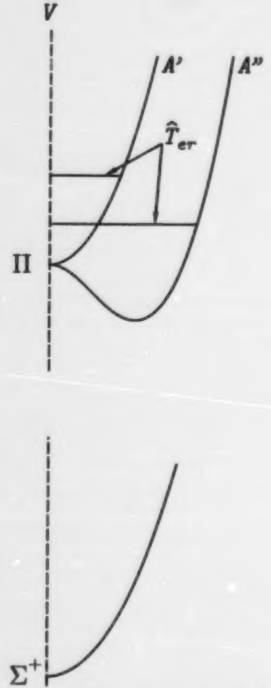

Fig. 13-5. The lowest bending potential energy curves of the singlet states of HCN. The abscissa is the bending coordinate $\rho = \pi - \angle(\text{HCN})$, the supplement of the bond angle, and the bond lengths are held constant. The left hand side of the diagram corresponds to linear configurations ($\rho = 0$). A pair of bending energy levels coupled by the vibronic kinetic energy $\hat{T}_{er}$ are marked to indicate schematically a Renner effect interaction.

As an example we consider the HCN molecule. In its linear configuration the ground electronic state of HCN is a Σ^+ state in the molecular point group $C_{\infty v}$, and the first excited electronic state is a Π state. At a bent configuration the HCN molecule has C_s point group symmetry and none of the electronic states are required by symmetry to be degenerate. The electronic Π state of linear HCN splits into an A' and an A'' electronic state of the bent molecule and the potential energy curves as a function of the angle of bend away from linearity are shown schematically in Fig. 13-5. For any molecule that can easily become linear, degenerate electronic states of the linear configuration are not required by symmetry to remain degenerate when the molecule is bent, and the potential energy curves that are degenerate in the linear configuration will split apart. However, since the states are degenerate at linearity they will usually be rather close together at near-linear configurations. This splitting of a degenerate electronic state upon bending, and the subsequent interaction between the levels of the states caused by the term T_{er} [see Eq. (13-143) and Fig. 13-5], is called the Renner effect.

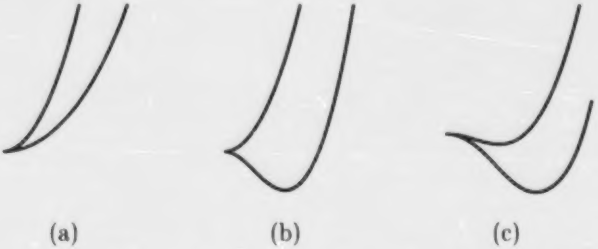

Fig. 13-6. Bending potential curves of triatomic molecules. For each of the three diagrams, the abscissa is the bending coordinate $\rho = \pi - \angle(\mathrm{ABC})$, the supplement of the bond angle for the triatomic molecule ABC. The bond lengths are held constant. The left hand side of each diagram corresponds to a linear configuration ($\rho = 0$). This shows three ways that an electronic degeneracy at the linear nuclear configuration can be resolved when the molecule is bent.

We use the angle ρ (the supplement of the bond angle) to indicate the deviation of the molecule from linearity, and for linear HCN it has the value 0. Any bending potential energy function has to be an even function of ρ since the sign of ρ cannot enter, and three of the ways that the the splitting of the bending potential energy curves of a degenerate electronic state (at linearity) can occur upon bending are indicated in Fig. 13-6; in each case the splitting is proportional to ρ^2. In the original paper of Renner (1934) the splitting as indicated in Fig. 13-6a was the only case considered. However, the first observation of the Renner effect [Dressler and Ramsay (1959)] turned out to be the situation depicted in Fig. 13-6c. To determine the species of the electronic states of the bent molecule from those of the linear molecule the appropriate correlation table of $\boldsymbol{D}_{\infty h} \rightarrow \boldsymbol{C}_{2v}$ and $\boldsymbol{C}_{\infty v} \rightarrow \boldsymbol{C}_s$ (given in Table B-3 of Appendix $\boldsymbol{B}$) can be used. We find that for the symmetries of the two electronic states of the bent molecule to correlate with a doubly degenerate symmetry in the linear configuration, these two states must necessarily transform according to the reducible representations $A' \oplus A''$ in $\boldsymbol{C}_s$, or they must transform according to one of the reducible representations $A_1 \oplus B_1$ or $A_2 \oplus B_2$ in $\boldsymbol{C}_{2v}$. That is, if we denote the symmetries of the two electronic states of the bent molecule as Γ_{elec} and

Γ'_{elec}, respectively, we have $\Gamma_{\mathrm{elec}} \otimes \Gamma'_{\mathrm{elec}} = A''$ for $\boldsymbol{C}_{\mathrm{s}}$ molecules and B_1 for $\boldsymbol{C}_{2\mathrm{v}}$ molecules.

For $\boldsymbol{C}_{2\mathrm{v}}$ molecules $\Gamma_{\mathrm{elec}} \otimes \Gamma'_{\mathrm{elec}} = B_1$ in the Renner effect and Eq. (13-165) is satisfied for $\alpha = z$, where the z axis becomes the molecular axis for linear configurations [Table A-5]. In a linear configuration, the electronic matrix element in Eq. (13-164) is given by

$$\left\langle \Phi_{\mathrm{elec}}^{(e,S,m_S)} \middle| \hat{L}_z \middle| \Phi_{\mathrm{elec}}^{(e',S,m_S)} \right\rangle = i\hbar\Lambda \qquad (13\text{-}173)$$

where the integer Λ, which defines the projection of the electronic angular momentum on the z axis, has the value 1 for a Π electronic state, 2 for a Δ state, and so on. When the molecule is in a bent configuration the matrix element will differ from the value given in Eq. (13-173). It should be noticed that this value depends on the relative phases chosen for the two electronic wavefunctions; we give here the result obtained with the customary phase choice. For $\alpha = z$, the interaction matrix element in Eq. (13-164) will contain the rotational matrix element $\langle \Phi_{\mathrm{rot}} | \hat{J}_z | \Phi'_{\mathrm{rot}} \rangle$. It is customary to take the rotational basis functions to be $\Phi_{\mathrm{rot}} = |J, k, m\rangle$, where $\hbar k$ is the projection of the angular momentum on the z axis as discussed in Chapter 11. In such a basis the interaction matrix elements will have $\Delta k = 0$ (see Table 11-1) and be proportional to $k = k'$.

The operator $\hat{T}_{\mathrm{ev}}$ in Eq. (13-142) does not give rise to large interaction matrix elements between the Renner electronic states. The term $\mu_{zz} \hat{p}_z \hat{L}_z$ in $\hat{T}_{\mathrm{ev}}$ vanishes for triatomic molecules. Formally, the vibrational angular momentum $\hat{p}_z$ has the same symmetry as $\hat{L}_z$, B_1 for $\boldsymbol{C}_{2\mathrm{v}}$ molecules and A'' for $\boldsymbol{C}_{\mathrm{s}}$ molecules. That is, it has negative parity. On the other hand it depends on the vibrational coordinates only and they all have positive parity. Thus $\hat{p}_z = 0$.

As a result of the above considerations the interaction matrix elements of $\hat{T}_{\mathrm{er}}$ vanish for $k = 0$ so that levels with $J = 0$ would appear to be unaffected by the Renner interaction. However, for $\Lambda \neq 0$ it is necessary to consider also the term $\hat{T}_{\mathrm{ee}}$ from Eq. (13-144). For $\alpha = \beta = z$, the matrix elements arising from this term will contain electronic integrals, which in the linear configuration are given by

$$\left\langle \Phi_{\mathrm{elec}}^{(e,S,m_S)} \middle| \hat{L}_z^2 \middle| \Phi_{\mathrm{elec}}^{(e,S,m_S)} \right\rangle = \left\langle \Phi_{\mathrm{elec}}^{(e',S,m_S)} \middle| \hat{L}_z^2 \middle| \Phi_{\mathrm{elec}}^{(e',S,m_S)} \right\rangle = \hbar^2\Lambda^2. \qquad (13\text{-}174)$$

The dominant effect of the term $\hat{T}_{\mathrm{ee}}$ is thus to add to the potential energy function for the two electronic states a mass-dependent pseudopotential term that will affect all rovibronic energy levels, including those with $J = 0$. For the the electronic state $\Phi_{\mathrm{elec}}^{(e,S,m_S)}$ this term is given by

$$V_\Lambda^{(e)} = \frac{1}{2}\mu_{zz}\hbar^2 \left\langle \Phi_{\mathrm{elec}}^{(e,S,m_S)} \middle| \hat{L}_z^2 \middle| \Phi_{\mathrm{elec}}^{(e,S,m_S)} \right\rangle, \qquad (13\text{-}175)$$

with an analogous expression for the electronic state $\Phi_{\mathrm{elec}}^{(e',S,m_S)}$. In Eq. (13-175), both μ_{zz} and the electronic integral $\left\langle \Phi_{\mathrm{elec}}^{(e,S,m_S)} \middle| \hat{L}_z^2 \middle| \Phi_{\mathrm{elec}}^{(e,S,m_S)} \right\rangle$ are functions of the nuclear coordinates. The pseudopotentials $V_\Lambda^{(e)}$ and $V_\Lambda^{(e')}$ will be most important at linear configurations or configurations close to linearity, since the function μ_{zz} is singular at linearity. For ρ near 0, i.e., for configurations near linearity, this function is given by

$$\mu_{zz} \approx \frac{f_{zz}(r_{12}, r_{23})}{\rho^2}, \tag{13-176}$$

where f_{zz} is a function of r_{12} and r_{23}, the two bond lengths of the ABC molecule. Because of the singularity of μ_{zz} at linearity, the approximation of setting it equal to the constant value μ_{zz}^e [in Eqs. (13-164) and (13-170)] does not lead to a satisfactory theoretical treatment of the Renner effect. The dependence of μ_{zz} on the bending coordinate must be considered explicitly. There exist a number of successful methods for calculating the rovibronic energies associated with electronic states subject to the Renner effect as detailed in the Bibliographical Notes.

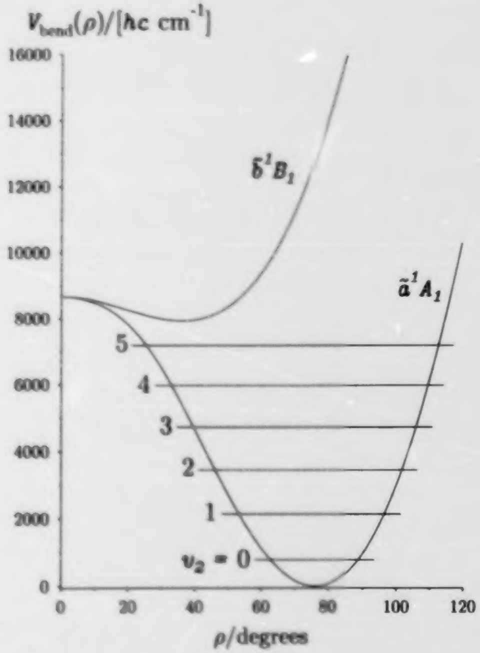

Fig. 13-7. Bending potential curves for the lowest singlet electronic states of the methylene radical CH_2 [from Jensen and Brumm (1996)]. The abscissa is the bending coordinate $\rho = \pi - \angle(\mathrm{HCH})$, the supplement of the bond angle. The bond lengths are held constant. For the $\tilde{a}\,^1A_1$ state the energies of the $(0, v_2, 0)$ vibrational states are indicated. The equilibrium configuration in the $\tilde{X}\,^3B_1$ electronic ground state of CH_2 corresponds to an energy approximately 3200 cm^{-1} below the $\tilde{a}\,^1A_1$ equilibrium energy [see Fig. 13-14]. For clarity, we omit the $\tilde{X}\,^3B_1$ state here.

The $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ electronic states of the methylene radical CH_2 provide an example of the Renner effect; they are degenerate as a $^1\Delta_g$ state ($\Lambda = 2$) at linearity. In Fig. 13-7 we show the bending potential curves for these states [from Jensen and Brumm (1996)] with the energies for the $(0, v_2, 0)$ vibrational states with $v_2 \leq 5$ (ν_2 is the bending vibrational mode) indicated for the $\tilde{a}$ state. These vibrational states have been characterized experimentally, and their rotational structure has been analyzed [see Hartland, Qin, and Dai (1995) and references therein]. One of the most dramatic effects of Renner interaction in a bent molecule such as CH_2 is the so-called "reordering" of the K_a rotational structure in the lower Renner component near the barrier to linearity. The interaction between the two electronic states lowers the $K_a > 0$ energies below the barrier to linearity in the lower Renner component, and the effect is strongest for the vibrational states close to the top of the barrier, since these states are energetically closest to their interaction partners in the upper Renner component. In $\tilde{a}\,^1A_1$ CH_2, the reordering causes an irregular variation of the effective A rotational constant, $A_{\rm eff}$, with v_2. For CH_2, the A rotational constant is the Z parameter of the Watsonian $\tilde{H}_{\rm rot}$ in Eq. (13-126), whose diagonal matrix elements contain a term $A\,K_a^2$. The rotational energy levels in the $(0, v_2, 0)$ vibrational states of $\tilde{a}\,^1A_1$ CH_2 have been fitted with a model that did not take into account the Renner interaction, and therefore the least squares fits did not yield the true A values for these vibrational states. Instead, "effective" A-values $A_{\rm eff}$ were obtained. They are effective in the sense that they have absorbed the effect of the Renner interaction. In Fig. 13-8, we show values of $A_{\rm eff}$ for the $(0, v_2, 0)$ vibrational states, obtained by fitting to experimentally observed data. For an isolated electronic state whose vibrational levels are not perturbed by resonances, we would expect $A_{\rm eff}$ to vary approximately linearly with v_2 [see, for example, Papoušek and Aliev (1982)], and this behavior is indeed confirmed by the experimental measurements for $v_2 \leq 4$. The (0,5,0) vibrational state, however, is very close to the top of the barrier to linearity [Fig. 13-7], so that in this state, the Renner interaction is sufficiently strong to cause a sudden drop in $A_{\rm eff}$ relative to the value for the $v_2 = 4$ state. The reordering has also been observed in the $\tilde{a}\,^3A_2 \leftarrow \tilde{X}\,^1\Sigma_g{}^+$ absorption spectrum of CS_2 [Jungen, Malm, and Merer (1973)], and in the $\tilde{A}\,^2A_1 \leftarrow \tilde{X}\,^2B_1$ emission spectrum of NH_2 [Vervloet (1988)].

If the barrier to linearity in the lower Renner component is small, the reordering can take place in the lowest bending states. This happens in the $\tilde{X}\,^2A_1$ and $\tilde{A}\,^2B_1$ electronic states of the CH_2^+ molecular ion. These states are degenerate as a $^2\Pi$ state ($\Lambda = 1$) at linearity. Their potential energy surfaces have been calculated *ab initio* by Kraemer, Jensen, and Bunker (1994). The calculated potential surfaces were adjusted very slightly to reproduce the one vibrational energy known experimentally for CH_2^+, the ν_3 energy in the $\tilde{X}\,^2A_1$ state measured by Rösslein, Gabrys, Jagod, and Oka (1992). In Fig. 13-9, we show the bending potentials obtained from the adjusted potential energy surfaces. Jensen, Brumm, Kraemer, and Bunker (1995b) have calculated the lowest rovibronic energies for $\tilde{X}\,^2A_1$ and $\tilde{A}\,^2B_1$ CH_2^+ from these potential en-

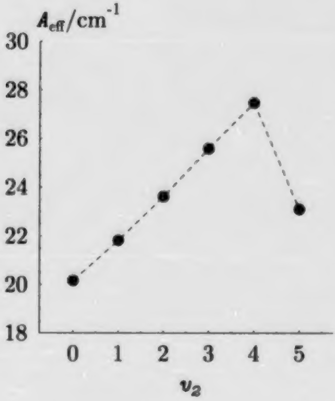

Fig. 13-8. Experimentally determined A_{eff} constants for the $(0, v_2, 0)$ vibrational states of $\tilde{a}\,^1A_1$ CH_2. The values are taken from Petek, Nesbitt, Moore, Birss, and Ramsay (1987), Xie, Harkin, and Dai (1990), and Hartland, Qin, and Dai (1995).

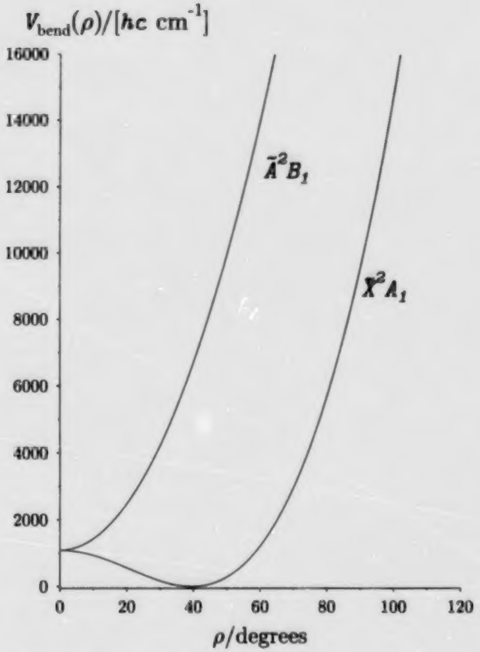

Fig. 13-9. Bending potential curves for the lowest electronic states of the CH_2^+ molecular ion. The abscissa is the bending coordinate $\rho = \pi - \angle(\mathrm{HCH})$, the supplement of the bond angle. The bond lengths are held constant.

ergy surfaces by using the theoretical approach of Jensen, Brumm, Kraemer, and Bunker (1995a). We have used the calculated energies to construct the term value diagrams shown in Figs. 13-10 and 13-11.

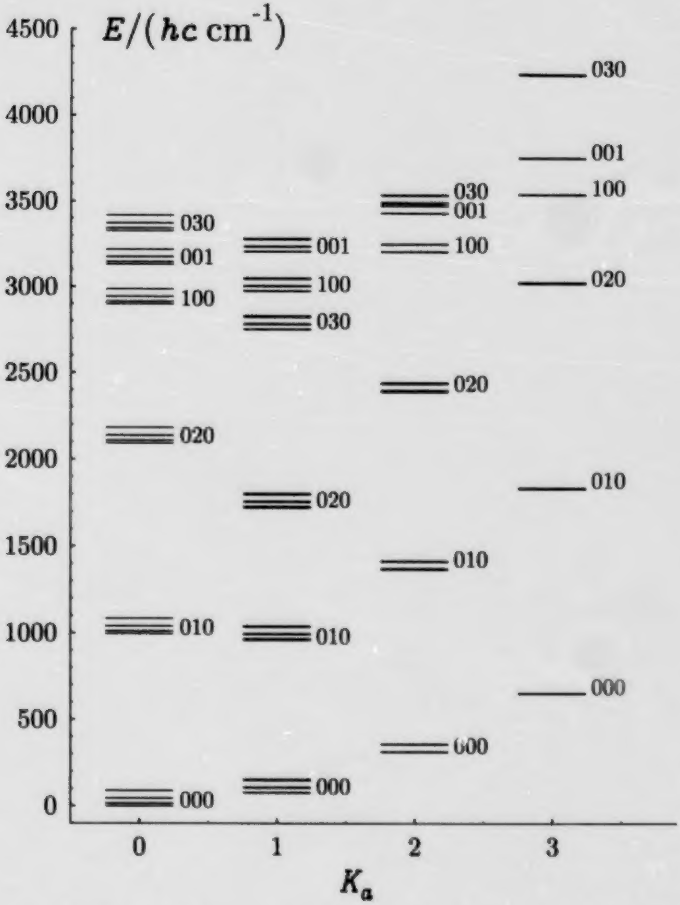

Fig. 13-10. Term level diagram for $\tilde{X}\,^2A_1$ CH_2^+. The energies are labeled by the vibrational quantum numbers $v_1v_2v_3$. The energies with common values of $v_1v_2v_3$ have different values of $N = K_a, K_a + 1, \ldots, 3$, and $J = |N - 1/2|$ or $N + 1/2$.

Since the electronic states under consideration for CH_2^+ have $S = 1/2$, the rovibronic levels in Figs. 13-10 and 13-11 are labeled by the quantum number N, the rovibronic angular momentum quantum number here, and $J = |N - 1/2|$ or $N + 1/2$; we also use the usual quantum numbers K_a, K_c, v_1, v_2 and v_3. The quantum number v_2 is that appropriate for a bent triatomic molecule [see Chapter 17]. We plot the energies with $N \leq 3$ against their K_a values. On the scale of the figures, the energies with common values of $v_1v_2v_3$ [but with different values of $N = K_a, K_a + 1, \ldots, 3$, and $J = |N - 1/2|$ or $N + 1/2$]

lie close together, and we label them by their value of $v_1v_2v_3$. Figure 13-10 shows that in the $\tilde{X}\,^2A_1$ electronic state of CH_2^+ energy reordering takes place already in the $v_2 = 1$ state, where the $K_a = 1$ energies are slightly below the $K_a = 0$ energies. In the $v_2 = 2$ and 3 states the $K_a = 1$ energies are far below the $K_a = 0$ ones. At higher K_a, however, the energy increases with K_a because of the $A\,K_a^2$ term in the diagonal matrix elements of the Watsonian. For K_a sufficiently large this term "wins" over the Renner interaction which tends to lower the high-K_a energies.

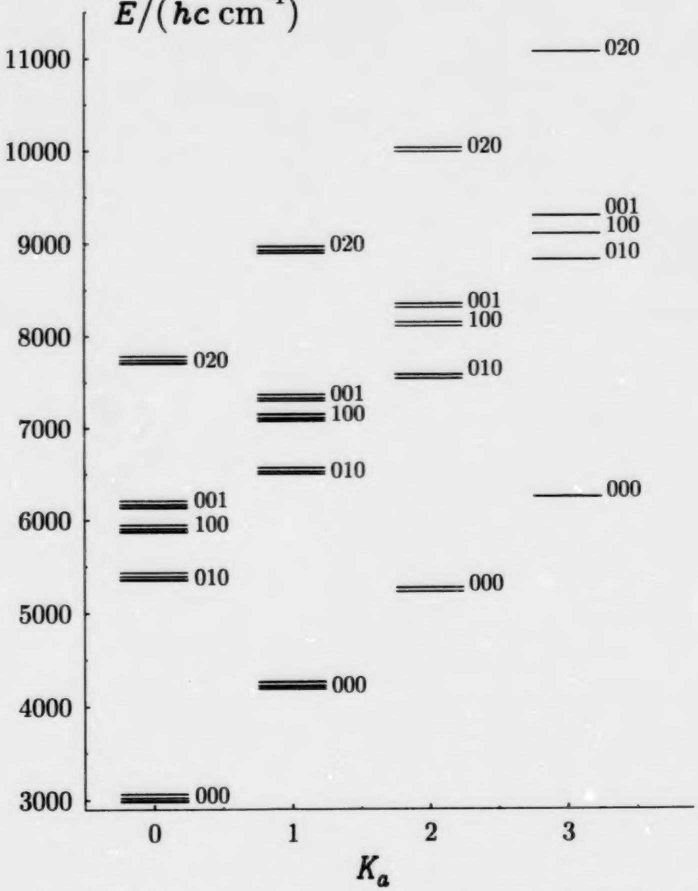

Fig. 13-11. Term level diagram for $\tilde{A}\,^2B_1$ CH_2^+. The energies are labeled by the vibrational quantum numbers $v_1v_2v_3$. The energies with common values of $v_1v_2v_3$ have different values of $N = K_a, K_a + 1, \ldots, 3$, and $J = |N - 1/2|$ or $N + 1/2$. The zero of energy is the $J = 1/2$, $N = 0$ level in the vibrational ground state of $\tilde{X}\,^2A_1$ CH_2^+ [Fig. 13-10].

In the $\tilde{A}\,^2B_1$ electronic state [Fig. 13-11] there is no energy reordering. The energies increase approximately linearly with K_a which is the behavior expected for a linear molecule [see Chapter 17]. The $\tilde{A}$ state levels are perturbed by the $\tilde{X}$ state levels, but some of the perturbing levels are above the perturbed level, and some are below it. Hence the effect of the perturbation cancels out to a large extent, and a regular energy level pattern is obtained. On the other hand, the $\tilde{X}$ state rovibronic levels are perturbed almost entirely by $\tilde{A}$ state levels that are above, and this leads to the energy reordering. For consistency between Figs. 13-10 and 13-11, we have labeled the energies in both of them by v_2, the bending quantum number as defined for a bent triatomic molecule. The bending quantum number as defined for a linear triatomic molecule is

$$v_2^{\text{linear}} = 2v_2 + |K_a \pm \Lambda|, \tag{13-177}$$

where the plus sign applies to the upper Renner component and the minus sign to the lower component [see, for example, Jensen, Brumm, Kraemer, and Bunker (1995a)]. It would have been more appropriate to label the levels of the $\tilde{A}$ state in Fig. 13-11 by v_2^{linear}.

13.4.2 The Jahn-Teller effect

A pair of electronic states of a polyatomic molecule that are degenerate at a particular symmetrical nonlinear nuclear configuration will always have their degeneracy split by some nuclear distortion that reduces the point group symmetry [Jahn and Teller (1937)]. This is the *static* Jahn-Teller effect, and the minimum in the lower of the two potential surfaces so obtained will be at a nuclear configuration of lower symmetry. At the symmetrical nuclear configuration the two potential energy surfaces will intersect at a *conical intersection*. Within the Born-Oppenheimer approximation each potential surface will have its own rotation-vibration energy levels, and the *dynamic* Jahn-Teller effect [Herzberg (1991b), page 54] occurs when there is interaction between the rotation-vibration levels of the two electronic states. The combination of the splitting of the electronic degeneracy by nuclear distortion, and the interaction between the levels of each electronic state, can be simply called *the* Jahn-Teller effect. The appropriate MS group to use for this situation is that appropriate for the symmetrical nuclear arrangement at which the molecule has to be a symmetric or spherical top. The zero order model used is of two degenerate harmonic potential energy surfaces with their common minimum at the symmetrical nuclear configuration; the static and dynamic Jahn-Teller effects are then treated together.

A well-studied example of a molecule exhibiting the Jahn-Teller effect is the methoxy radical CH_3O [see, for example, Powers, Pushkarsky, and Miller (1997a), Geers, Kappert, Temps, and Sears (1993), and references therein]; its MS group is $\boldsymbol{C}_{3v}(M)$ [Table A-6] and its electronic ground state is ^2E. If we carry out *ab initio* calculations (see Chapter 9) for this molecule in order to determine the electronic energies and wavefunctions, we can classify the electronic wavefunctions for a given, fixed nuclear geometry in the point group appropriate for that geometry. That is, in the high-symmetry nuclear geometries with $\boldsymbol{C}_{3\text{v}}$ point group symmetry, the electronic ground state wavefunctions of CH_3O will be doubly degenerate and transform according to the E irreducible representation of $\boldsymbol{C}_{3\text{v}}$. We denote by $\left(\Phi_{\text{elec}}^{(a)}, \Phi_{\text{elec}}^{(b)}\right)$ a pair of real electronic wavefunctions of E symmetry, calculated at a nuclear geometry with $\boldsymbol{C}_{3\text{v}}$ point group symmetry. To determine the transformation properties of $\left(\Phi_{\text{elec}}^{(a)}, \Phi_{\text{elec}}^{(b)}\right)$ in the molecular symmetry group $\boldsymbol{C}_{3\text{v}}(\text{M})$ (these transformation properties are identical to those in the point group $\boldsymbol{C}_{3\text{v}}$) it is sufficient to determine the transformation properties under the generating operations (123) and (23)*. Choosing the (a) and (b) wavefunctions so that they transform as T_x and T_y, respectively, and forming the linear combinations

$$\Phi_{\text{elec}}^{(\pm)} = \frac{1}{\sqrt{2}}\left(\Phi_{\text{elec}}^{(a)} \pm i\,\Phi_{\text{elec}}^{(b)}\right), \tag{13-178}$$

which are analogous to the $(Q_t{}^{+}, Q_t{}^{-})$ defined in Table 12-4, the transformation properties are

$$(123)\,\Phi_{\text{elec}}^{(\pm)} = \exp(\mp i2\pi/3)\,\Phi_{\text{elec}}^{(\pm)} \tag{13-179}$$

and

$$(23)^{*}\,\Phi_{\text{elec}}^{(\pm)} = \Phi_{\text{elec}}^{(\mp)}. \tag{13-180}$$

In zero order the particular nuclear geometry of $\boldsymbol{C}_{3\text{v}}$ point group symmetry at which the electronic wavefunctions $\left(\Phi_{\text{elec}}^{(a)}, \Phi_{\text{elec}}^{(b)}\right)$ are obtained corresponds to all normal coordinates being zero. We consider a displaced geometry, close to the $\boldsymbol{C}_{3\text{v}}$ one, in which only a pair of degenerate normal coordinates (Q_{ta}, Q_{tb}) of species E in $\boldsymbol{C}_{3\text{v}}$ are nonzero. The electronic energies and wavefunctions at this displaced geometry are obtained by diagonalizing a matrix representation of the electronic Hamiltonian $\hat{H}_{\text{elec}}$ [Eq. (9-63)] in the basis functions $\left(\Phi_{\text{elec}}^{(+)}, \Phi_{\text{elec}}^{(-)}\right)$ given by Eq. (13-178); $\hat{H}_{\text{elec}}$ depends parametrically on the nuclear coordinates and we take the $\hat{H}_{\text{elec}}$ appropriate for the displaced geometry. If no other electronic states are energetically close to $\left(\Phi_{\text{elec}}^{(a)}, \Phi_{\text{elec}}^{(b)}\right)$, the electronic energies and wavefunctions at the displaced geometry can be obtained with good accuracy by this matrix diagonalization. The matrix elements are

$$\begin{aligned} V_{++} &= \int \Phi_{\text{elec}}^{(+)*}\hat{H}_{\text{elec}}\Phi_{\text{elec}}^{(+)}dV, \quad & V_{--} &= \int \Phi_{\text{elec}}^{(-)*}\hat{H}_{\text{elec}}\Phi_{\text{elec}}^{(-)}dV, \\ V_{+-} &= \int \Phi_{\text{elec}}^{(+)*}\hat{H}_{\text{elec}}\Phi_{\text{elec}}^{(-)}dV, \quad & V_{-+} &= \int \Phi_{\text{elec}}^{(-)*}\hat{H}_{\text{elec}}\Phi_{\text{elec}}^{(+)}dV, \end{aligned} \tag{13-181}$$

where integration is over the electronic coordinates only and dV is the volume element in these coordinates. The vanishing integral rule cannot be directly applied to the integrals of Eq. (13-181) because they are not pure numbers, but functions of the nuclear coordinates, i.e., of (Q_{ta}, Q_{tb}). From the fact that H_{elec} is invariant under the operations of the MS group, and from Eqs. (13-179)-(13-180), we deduce that the operation (123) leaves V_{++} and V_{--} unchanged, it multiplies V_{+-} by ω^2, and V_{-+} by ω [where $\omega = \exp(i2\pi/3)$]. The effect of the operation $(23)^*$ is to interchange V_{++} and V_{--}, and to interchange V_{+-} and V_{-+}. We expand the matrix elements in Eq. (13-181) as Taylor series, truncated after second order, in the coordinates $(Q_t{}^+, Q_t{}^-)$ defined in Table 12-4; it can be seen from that table that the following expansions comply with the symmetry conditions just derived:

$$V_{++} = V_{--} = V_0 + V_{++}^{+-}\, Q_t{}^+ Q_t{}^-, \tag{13-182}$$

$$V_{+-} = V_{+-}^{+}\, Q_t{}^+ + V_{+-}^{--}\, (Q_t{}^-)^2, \tag{13-183}$$

and

$$V_{-+} = V_{+-}^{+}\, Q_t{}^- + V_{+-}^{--}\, (Q_t{}^+)^2, \tag{13-184}$$

where V_0, V_{++}^{+-}, V_{+-}^{+}, and V_{+-}^{--} are molecular parameters, obtained by differentiation of the matrix elements in Eq. (13-181) with respect to $Q_t{}^+$ and $Q_t{}^-$. All four parameters are real since the matrix

$$\begin{bmatrix} V_{++} & V_{+-} \\ V_{-+} & V_{--} \end{bmatrix} \tag{13-185}$$

is Hermitian. The eigenvalues of this matrix are

$$\begin{aligned} V_\pm = {} & V_0 + V_{++}^{+-}\, Q_t^2 \\ & \pm Q_t \sqrt{\left(V_{+-}^{+}\right)^2 + \left(V_{+-}^{--}\right)^2 Q_t^2 + 2\, V_{+-}^{+}\, V_{+-}^{--}\, Q_t \cos 3\alpha_t}, \end{aligned} \tag{13-186}$$

where we have introduced the notation $(Q_{ta}, Q_{tb}) = (Q_t \cos\alpha_t, Q_t \sin\alpha_t)$ from Eqs. (11-146) and (11-147).

For small values of Q_t in Eq. (13-186) terms linear in Q_t will dominate over higher order terms, and we have $V_\pm = V_0 \pm |V_{+-}^{+}|\, Q_t$. Here, V_0 is the electronic energy at the geometry of C_{3v} point group symmetry [where $Q_{ta} = Q_{tb} = Q_t = 0$], and we see that $V_- < V_0$ for small displaced geometries since $Q_t > 0$. This is the effect of the *Jahn-Teller theorem*: If a molecule is found to have a degenerate electronic state at a geometry with symmetric top or spherical top point group symmetry, then there is always at least one non-totally symmetric normal coordinate Q that causes a splitting of the potential surfaces of first order[11] in Q so that the minimum is not at the high-symmetry geometry. For small values of Q_t the upper (V_+) and lower (V_-) potential energy surfaces are conical and touch at the symmetrical Q_t=0 configuration;

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[11] In contrast to the Renner effect for which the splitting is of second order in the deviation from linearity; see above.

this is a conical intersection. For larger displacements the higher order terms will take over and raise the electronic energy V_- above V_0. The energy at the minimum in V_- (occurring when $Q_t=Q_t^{\mathrm{min}}$ and $\alpha_t=\alpha_t^{\mathrm{min}}$) is lower than V_0, and this is called the ***Jahn-Teller instability***; the symmetrical configuration is unstable on the V_- surface. It is further seen that if we hold $Q_t=Q_t^{\mathrm{min}}$ and vary α_t from 0 to 2π, the potential surface will have three equivalent minima as discussed by Herzberg (1991b). The minima are caused by the $\cos 3\alpha_t$ term in Eq. (13-186). In general [Herzberg (1991b)], the Jahn-Teller effect will give rise to n symmetrically equivalent minima in the potential function if the high-symmetry geometry has a principal symmetry axis $\boldsymbol{C}_n$ [see Chapter 4] with n odd. In the case of an axis $\boldsymbol{C}_n$ with n even, there will be $n/2$ minima.

In Fig. 13-12, we show the potential energy surface V_- from Eq. (13-186), drawn as a function of (Q_{12a}, Q_{12b}) with the parameters given in Table III of Miller and Bondybey (1983) for the ν_{12} CCC bending vibration (of symmetry E' in $\boldsymbol{D}_{3\mathrm{h}}$) for the ground electronic state (a ${}^2E''$ state in $\boldsymbol{D}_{3\mathrm{h}}$) of the $\mathrm{C_6H_3F_3^+}$ molecular ion. The three equivalent minima [351 $\mathrm{cm^{-1}}$ below the energy at $Q_{12a} = Q_{12b} = 0$] are so shallow that they are not recognizable in the figure. They are made visible, however, in Fig. 13-13 where we draw contour lines for V_-.

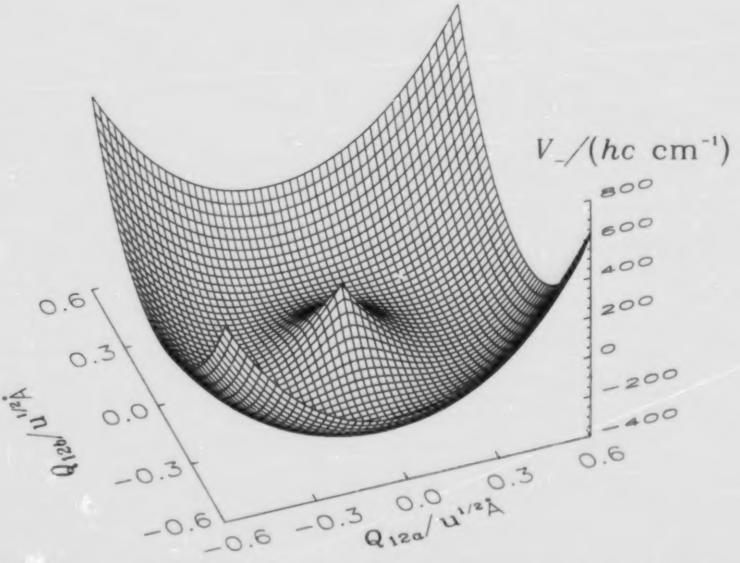

Fig. 13-12. The potential energy surface V_- from Eq. (13-186) [with $V_0 = 0$], drawn as a function of (Q_{12a}, Q_{12b}) with the parameters given in Table III of Miller and Bondybey (1983) for the ν_{12} CCC bending vibration of $\mathrm{C_6H_3F_3^+}$. At the central "tip", where all $Q_r = 0$, the energy is $V_0 = 0$, and V_- is degenerate with V_+. The energy lowering around the tip is due to the Jahn-Teller instability.

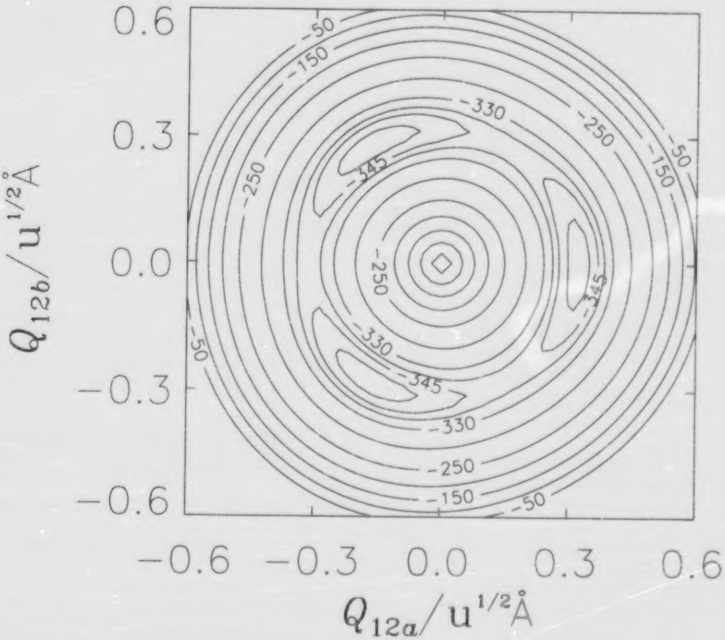

Fig. 13-13. Contour lines for the potential energy surface V_- from Eq. (13-186) [with $V_0 = 0$], taken to be a function of (Q_{12a}, Q_{12b}) with the parameters given in Table III of Miller and Bondybey (1983) for the ν_{12} CCC bending vibration of $C_6H_3F_3^+$ [see Fig. 13-12]. The function V_-/hc is expressed in units of cm^{-1}, and the contour lines are drawn at −350, −345, −340, −330, −300, −250, −200, −150, −100, and −50 cm^{-1}. The three equivalent minima (see text) are 351 cm^{-1} below the energy at $Q_{12a} = Q_{12b} = 0$.

To obtain $V_- < V_0$ for small Q_t we must have $V_{+-}^{+} \neq 0$. In our C_{3v} example above we assumed normal coordinates (Q_{ta}, Q_{tb}) of E symmetry; if there were none of this symmetry there would be no Jahn-Teller instability. For the parameter V_{+-}^{+} to be nonvanishing it is necessary that the molecule has (Q_t^+, Q_t^-) coordinates that transform under the operations in the MS group as the wavefunction products $\Phi_{\mathrm{elec}}^{(+)*}\Phi_{\mathrm{elec}}^{(-)}$ and $\Phi_{\mathrm{elec}}^{(-)*}\Phi_{\mathrm{elec}}^{(+)}$. That is, the coordinates (Q_t^+, Q_t^-) must belong to the same irreducible representations of the MS group as the electronic wavefunction products. If the two electronic functions $\left(\Phi_{\mathrm{elec}}^{(a)}, \Phi_{\mathrm{elec}}^{(b)}\right)$ span the degenerate irreducible representation Γ_{elec} in the MS group, then the wavefunction products $\Phi_{\mathrm{elec}}^{(+)*}\Phi_{\mathrm{elec}}^{(-)}$ and $\Phi_{\mathrm{elec}}^{(-)*}\Phi_{\mathrm{elec}}^{(+)}$ transform according to the symmetric product $[\Gamma_{\mathrm{elec}}]^2$ [Eq. (6-117)]. Thus, normal coordinates Q_r with symmetry Γ_r give rise to a Jahn-Teller instability if

$$[\Gamma_{\mathrm{elec}}]^2 - \Gamma^{(s)} \supset \Gamma_r. \qquad (13\text{-}187)$$

Normal coordinates satisfying Eq. (13-187) are said to be *Jahn-Teller ac-*

tive. For the ground electronic state of $C_6H_3F_3^+$ we have $\Gamma_{\text{elec}} = E''$, so that $[\Gamma_{\text{elec}}]^2 - \Gamma^{(s)} = E'$. Thus vibrations of species E' are Jahn-Teller active and the ν_{12} CCC bending vibration is such a vibration. It should be noted that $[\Gamma_{\text{elec}}]^2$ always contains the totally symmetric representation $\Gamma^{(s)}$ but, as indicated in Eq. (13-187), totally symmetric normal coordinates do not produce a Jahn-Teller instability. The products $\Phi_{\text{elec}}^{(+)*}\Phi_{\text{elec}}^{(+)}$ and $\Phi_{\text{elec}}^{(-)*}\Phi_{\text{elec}}^{(-)}$ are totally symmetric, and the condition $[\Gamma_{\text{elec}}]^2 \supset \Gamma^{(s)}$ only ensures that the two matrix elements V_{++} and V_{--} are nonvanishing.

If we define the phase factor $e^{i\theta} = V_{+-}/|V_{+-}|$, then the two vectors

$$\begin{bmatrix} e^{+i\theta/2}/\sqrt{2} \\ e^{-i\theta/2}/\sqrt{2} \end{bmatrix} \text{ and } \begin{bmatrix} ie^{+i\theta/2}/\sqrt{2} \\ -ie^{-i\theta/2}/\sqrt{2} \end{bmatrix} \tag{13-188}$$

are eigenvectors of the matrix in Eq. (13-185). In general the phase angle θ introduced here (which has nothing to do with the Euler angle θ) is a function of Q_{ta} and Q_{tb} (or, equivalently, of Q_t and α_t). Thus, in the approximation employed here, the eigenfunctions of $\hat{H}_{\text{elec}}$ at the displaced geometry in question can be expressed as

$$\Psi_{\text{elec}}^{(a)} = \frac{1}{\sqrt{2}}\left(e^{+i\theta/2}\Phi_{\text{elec}}^{(+)} + e^{-i\theta/2}\,\Phi_{\text{elec}}^{(-)}\right) \tag{13-189}$$

and

$$\Psi_{\text{elec}}^{(b)} = \frac{i}{\sqrt{2}}\left(e^{+i\theta/2}\Phi_{\text{elec}}^{(+)} - e^{-i\theta/2}\,\Phi_{\text{elec}}^{(-)}\right). \tag{13-190}$$

Viewed as functions of Q_t and α_t, $\Psi_{\text{elec}}^{(a)}$ and $\Psi_{\text{elec}}^{(b)}$ are "smoothly varying" in the sense discussed by Mead (1992). Their phases [i.e., the factors of $\exp(\pm i\theta/2)$ and i in Eq. (13-188)] have been chosen so that when we vary the nuclear coordinates Q_t and α_t, the eigenfunctions change in a continuous manner. The smooth variation is obtained by requiring the functions to be invariant under time reversal [see Chapter 7], i.e., to be real. The reader can easily verify that since the two functions $\Phi_{\text{elec}}^{(a)}$ and $\Phi_{\text{elec}}^{(b)}$ are real, then $\Psi_{\text{elec}}^{(a)}$ and $\Psi_{\text{elec}}^{(b)}$ are real also.

Let us consider a displaced geometry with a small, nonzero value of Q_t [i.e., a displaced geometry close to the high-symmetry geometry]. For Q_t small, the linear term in Eq. (13-183) will dominate over the quadratic term, and we have $V_{+-} = V_{+-}^{+}\,Q_t{}^{+} = V_{+-}^{+}\,Q_t \exp(i\alpha_t)$. That is, in this situation $\theta = \alpha_t$ since V_{+-}^{+} is real. If we now hold Q_t fixed at its small value and let $\theta = \alpha_t \rightarrow \alpha_t + 2\pi$, it is seen that we cause the eigenfunctions in Eq. (13-189) and (13-190) to change sign. In nuclear coordinate space a closed path is followed and the path encloses the point ($Q_t = 0$) where the two electronic surfaces are degenerate. At the end of the path the nuclear coordinates have returned to their original values, but the electronic wavefunctions are the original wavefunctions multiplied by a phase factor of $-1 = \exp(i\pi)$. This is a particular example of *geometric phase* [or Berry phase; Berry (1984)]. Geometric phase is treated in detail in the review by Mead (1992).

The geometric phase of the electronic wavefunction encountered here was discussed for the first time by Longuet-Higgins, Öpik, Pryce, and Sack (1958) [see also Herzberg and Longuet-Higgins (1963)]. In the Born-Oppenheimer approximation, the double valuedness "problem" [i.e., the fact that $\Psi_{\text{elec}}^{(a)}$ and $\Psi_{\text{elec}}^{(b)}$ have two values, differing by their signs, at any point in nuclear coordinate space] disappears when we multiply these electronic wavefunctions by appropriate vibrational wavefunctions. This is because the latter must also change sign when we traverse the closed paths in nuclear coordinate space just described in order that the vibronic wavefunctions be single valued functions, as they must, of the nuclear coordinates. An exactly analogous double valued wavefunction problem occurs when we separate single valued rotation-torsion wavefunctions into rotation and torsion wavefunctions for dimethylacetylene (see Chapter 15). There are important consequences of the geometric phase and one must be careful to perform theoretical calculations in an appropriate manner for Jahn-Teller systems. For example, the requirement that the vibrational wavefunctions change sign has an important implication on the energy level ordering of the vibronic states in a Jahn-Teller system [see, for example, O'Brien (1964) and Ham (1987)]. As another example, the geometric phase induced by the conical intersection between the two lowest electronic states of the $H + H_2$ system has to be included in the calculation of product rotational state distributions and integral cross sections for the $H + H_2$, $D + H_2$ and $H + D_2$ reactions in order to get agreement with experiment [Wu and Kuppermann (1993,1995)].

In practice, the vibronic energies for a electronic state exhibiting the Jahn-Teller effect are calculated by diagonalizing a matrix representation of the Hamiltonian [see, for example, the review by Miller and Bondybey (1983)]

$$\hat{H}_{\text{JT}} = \hat{T}_{\text{vib}} + \hat{H}_{\text{elec}} \tag{13-191}$$

[where T_{vib} is the kinetic energy of the nuclei defined in Eq. (10-144)] constructed in a basis of single valued functions

$$\left|\Phi_{\text{elec}}^{(a)}\right\rangle |v_1\rangle\, |v_2\rangle \ldots |v_q\rangle\, |v_{q+1}, l_{q+1}\rangle\, |v_{q+2}, l_{q+2}\rangle \ldots$$

and

$$\left|\Phi_{\text{elec}}^{(b)}\right\rangle |v_1\rangle\, |v_2\rangle \ldots |v_q\rangle\, |v_{q+1}, l_{q+1}\rangle\, |v_{q+2}, l_{q+2}\rangle \ldots .$$

The vibrational basis functions are those introduced in Eq. (12-73); the normal coordinates defining the harmonic oscillator eigenfunctions are all zero at the highly symmetrical geometry where the electronic functions $\left(\Phi_{\text{elec}}^{(a)}, \Phi_{\text{elec}}^{(b)}\right)$ are obtained. In setting up the matrix representation of $\hat{H}_{\text{JT}}$, the matrix elements of $\hat{H}_{\text{elec}}$ between the electronic basis functions $\Phi_{\text{elec}}^{(a)}$ and $\Phi_{\text{elec}}^{(b)}$ are expanded in terms of these normal coordinates as indicated in Eqs. (13-182)-(13-184), and the matrix elements of these expansions between the harmonic oscillator eigenfunctions can be calculated using the results of Table 11-3 [see also Eqs. (16) and (17), together with Table I, of Miller and Bondybey (1983)]. The electronic matrix elements coupling $\Phi^{(a)}_{\text{elec}}$ and $\Phi^{(b)}_{\text{elec}}$ are power series in the normal coordinates [see Eq. (13-184)], and the linear terms in these series are said to cause ***linear Jahn-Teller coupling*** whereas the quadratic terms are said to cause ***quadratic Jahn-Teller coupling***.

The rotational energy structure in vibronic states of symmetric top molecules subject to the Jahn-Teller effect has been treated by many authors; we give a selection of papers in the Bibliographical Notes. In contrast to the Renner effect, which is essentially a ***rovibronic*** interaction capable of perturbing significantly the rotational energy level patterns in the vibronic states affected by it [see Figs. 13-10 and 13-11], the perturbations resulting from the Jahn-Teller effect are predominantly ***vibronic***. The rotational energies in Jahn-Teller vibronic states are usually well described by an effective rotational Hamiltonian obtained by averaging the rotational kinetic energy operator over the eigenfunctions of $\hat{H}_{\text{JT}}$. In a treatment of this type Brown (1971) determines the dominant effect on the rotational energy levels of a symmetric top to be an apparent change in $\zeta^z_{ta,tb}$, the Coriolis coupling parameter [Eq. (10-152)] associated with the Jahn-Teller active normal mode ν_t. In the expression for the rotational energies $\zeta^z_{ta,tb}$ is replaced by an effective Coriolis coupling parameter ζ_{ev}, where $\zeta_{\text{ev}} - \zeta^z_{ta,tb}$ depends on the vibronic matrix elements of $\hat{L}_z$ [see Eq. (29) of Brown (1971)]. Hougen (1980a) and Watson (1984) detail further the derivation of appropriate effective rotational Hamiltonians for symmetric top molecules, and Watson extends the treatment to spherical tops.

Liu and Miller (1992) give a general discussion of the technique for deriving totally symmetric terms [with expansion coefficients that can subsequently be fitted to experiment] in the effective rotational Hamiltonian; their work is based on a general theorem concerning the matrix elements of operators between components of a degenerate state. A proof of the theorem is outlined by Watson (1974). The proof makes use of the combined effects of time reversal (see Chapter 7) and Hermitian conjugation [see Eq. (6-153)]. We consider an operator $\hat{O}$ [with symmetry Γ_O in the MS group] together with a set of functions Ψ_{im}, $m = 1, 2, 3, \ldots, l_i$ [see Chapter 6], which span a degenerate irreducible representation Γ_i as described by Eq. (6-66). In order for the matrix elements $\left\langle \Psi_{im} \middle| \hat{O} \middle| \Psi_{im'} \right\rangle$ to be non-vanishing certain conditions must be fulfilled by the irreducible representations Γ_i and Γ_O. These conditions are different for single valued[12] and double valued irreducible representations Γ_i, and they depend on the properties of the operator $\hat{O}$ under time reversal and Hermitian conjugation. The following symmetry conditions can be derived in order for the matrix element $\left\langle \Psi_{im} \middle| \hat{O} \middle| \Psi_{im'} \right\rangle$ to be non-vanishing:

---

[12] All the irreducible representations that we have encountered so far are single valued. We discuss *double valued* irreducible representations in connection with *double groups* in Chapters 15 and 18.

(A) $[\Gamma_i]^2 \supset \Gamma_O$ if Γ_i is single valued and $(\hat{\theta}\hat{O}\hat{\theta}^{-1})^\dagger = \hat{O}$, *or* if Γ_i is double valued and $(\hat{\theta}\hat{O}\hat{\theta}^{-1})^\dagger = -\hat{O}$.

(B) $\{\Gamma_i\}^2 \supset \Gamma_O$ if Γ_i is single valued and $(\hat{\theta}\hat{O}\hat{\theta}^{-1})^\dagger = -\hat{O}$, *or* if Γ_i is double valued and $(\hat{\theta}\hat{O}\hat{\theta}^{-1})^\dagger = \hat{O}$.

(C) $\Gamma_i^2 \supset \Gamma_O$ if $(\hat{\theta}\hat{O}\hat{\theta}^{-1})^\dagger \neq \pm\hat{O}$, regardless of whether Γ_i is single valued or double valued.

Here, $\{\Gamma_i\}^2$ is the antisymmetric product [Eq. (6-118)], Γ_i^2 is the simple product $\Gamma_i \otimes \Gamma_i = [\Gamma_i]^2 \oplus \{\Gamma_i\}^2$, $\hat{\theta}$ is the time reversal operator, and a superscript $\dagger$ denotes Hermitian conjugation.

13.5 RYDBERG STATES

Rydberg states are special electronic states and for them, just as for the electronic states involved in the Renner effect or Jahn-Teller effect, there are systematic degeneracies and near degeneracies that make it appropriate to calculate energies from a starting point other than the Born-Oppenheimer approximation. The Born-Oppenheimer approximation is not generally valid for such states. We can describe a Rydberg state of a molecule M as being an electronic state in which a *Rydberg electron* orbits, at a distance large compared to molecular dimensions, the ionic molecule M^+ which is called the *core*. Since the core is itself a molecular system it will be in a state labeled by quantum numbers, and because of this we say that the core has *structure*. The quantum nature of electronic motion, and the requirements of the Pauli exclusion principle, clearly make this a rather crude picture. It is helpful, however, in understanding the model used here to obtain the electronic energies, which is very different from that used for valence electronic states. In Rydberg states when the Rydberg electron is far from the core the interaction between electron and core is independent of the structure of the core. It is essentially the same as the electrostatic interaction between the electron and proton in a hydrogen atom, and we can use the energy level pattern and the form of the electronic wavefunctions of the hydrogen atom as a zero order way of understanding Rydberg states. This is one of the fundamental ideas behind *Quantum Defect Theory* (QDT) or the more general *Multichannel Quantum Defect Theory* (MQDT), that we briefly introduce in the present section. The technique does not involve the diagonalization of a Hamiltonian matrix using a basis set as we have become accustomed to. Our discussion is based on the introductory account by Ross (1991).

For a hydrogen atom all states are Rydberg states. The bound state energies are given by

$$\epsilon = -\frac{E_\mathrm{h}}{2n^2}; \quad n = 1, 2, 3, 4, \dots, \tag{13-192}$$

where the hartree E_h is defined in Eq. (9-85), and we have neglected the difference between m_e, the mass of the electron, and the reduced mass $\mu_{\text{red}} = m_p m_e/(m_p + m_e)$, where m_p is the mass of the proton. The energy zero corresponds to the electron and proton being at rest infinitely separated. For the purpose of later manipulations we define ν as

$$\nu = \sqrt{-\frac{E_h}{2\epsilon}}, \tag{13-193}$$

so that for the hydrogen atom we simply have $\nu = n = 1, 2, 3, 4, \ldots$.

The internal motion of a hydrogen atom involves the coordinates (r, θ, ϕ) defined in Eqs. (9-10)-(9-12). The wavefunction for the internal motion is $\Phi_{\text{int}}(r, \theta, \phi) = (1/r)\Phi_{\nu\ell m}(r, \theta, \phi) = (1/r)\psi_\ell(\nu, r)Y_{\ell m}(\theta, \phi)$, where $Y_{\ell m}(\theta, \phi)$ is a spherical harmonic function; for a hydrogen atom, $\ell = 0, 1, 2, \ldots, \nu - 1$, and $m = -\ell, -\ell + 1, \ldots, \ell$. The *radial function* $\psi_\ell(\nu, r)$ satisfies the equation

$$\left[-\frac{\hbar^2}{2m_e}\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2}\right) + (V(r) - \epsilon)\right]\psi_\ell(\nu, r) = 0 \tag{13-194}$$

where

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}. \tag{13-195}$$

The eigenfunction $\Phi_{\nu\ell m}(r, \theta, \phi)$ is normalized with the volume element $\sin\theta\, dr\, d\theta\, d\phi$, which differs from that $(r^2 \sin\theta\, dr\, d\theta\, d\phi)$ appropriate for $\Phi_{\text{int}}(r, \theta, \phi)$ because of the factor $(1/r)$ in the wavefunction definition.

For the Rydberg states of a sodium atom once the Rydberg electron is at a distance r_c, say, from the Na^+ core, the effects of its interaction with the electrons in the core can be neglected. Thus, for $r > r_c$ the interaction between the Rydberg electron and the core is described by Eq. (13-194). For $r < r_c$ it will be necessary to consider the interaction of the Rydberg electron with the Na nucleus and with the core electrons. In the region $r > r_c$ we take the complete wavefunction to be given by

$$\Phi_\ell(\nu, r, \omega) = \psi_\ell(\nu, r)\,\Phi^{(\ell)}_{\text{core}}(\omega), \tag{13-196}$$

where $\psi_\ell(\nu, r)$ is the radial part of the wavefunction for the Rydberg electron, and $\Phi^{(\ell)}_{\text{core}}(\omega)$ contains the angular part of the wavefunction for the Rydberg electron and the wavefunction specifying the structure of the core; ω is a shorthand notation for all degrees of freedom other than the radial degree of freedom of the Rydberg electron.

This theory can also be used to describe a collision between an electron and a Na^+ core. In this case the Rydberg electron (or the *collision electron*) and the core are initially separated by an infinite distance, and the ϵ is a positive energy in the ionization continuum of the sodium atom rather than a negative eigenvalue corresponding to a discrete bound state; it can in principle have any positive value. For the colliding electron we can also express the wavefunction for $r > r_c$ as given in Eq. (13-196), and we would obtain the radial function $\psi_\ell(\nu, r)$ by solving Eq. (13-194) for the known, fixed value of ϵ determined by the initial conditions of the collision.

For a given ϵ Eq. (13-194) is no longer an eigenvalue equation (the Schrödinger equation) but it is a standard second order differential equation for which the general structure of the solutions is well known [see, for example, Seaton (1983)]. A general solution (defined at all energies) can be written as the following linear combination of two linearly independent functions $f_\ell(\nu, r)$ and $g_\ell(\nu, r)$:

$$\psi_\ell(\nu, r) = \cos[\pi\mu_\ell]\, f_\ell(\nu, r) - \sin[\pi\mu_\ell]\, g_\ell(\nu, r), \qquad (13\text{-}197)$$

where we have expressed the coefficients of the two functions in terms of a parameter μ_ℓ which measures the extent of the mixing of $f_\ell(\nu, r)$ and $g_\ell(\nu, r)$. The function $\psi_\ell(\nu, r)$ [where ϵ is arbitrary] is known as a *channel function*. We do not go into the detailed form of $f_\ell(\nu, r)$ and $g_\ell(\nu, r)$; it suffices to say that $f_\ell(\nu, r)$ is non-singular at $r = 0$, whereas $g_\ell(\nu, r)$ is singular at this point. Further, it is known that for $\epsilon < 0$ and $r \to \infty$ the two functions can be approximated by

$$f_\ell(\nu, r) \approx \quad C(r) \sin[\pi(\nu - \ell)] \exp\left(\frac{r}{\nu a_0}\right) \qquad (13\text{-}198)$$

and

$$g_\ell(\nu, r) \approx -C(r) \cos[\pi(\nu - \ell)] \exp\left(\frac{r}{\nu a_0}\right), \qquad (13\text{-}199)$$

where the Bohr radius a_0 is defined in Eq. (9-84). The function $C(r)$ in Eqs. (13-198) and (13-199) is such that for $r \to \infty$, $|C(r)\exp[r/(\nu a_0)]| \to \infty$.

The theory discussed here describes in general a collision between an electron and a Na^+ core and is valid for any value of ϵ. However, it can also give us the energies of the bound Rydberg states of a sodium atom. The conditions for the Rydberg electron being in a bound state are $\epsilon < 0$ and

$$\psi_\ell(\nu, r) \to 0 \text{ for } r \to \infty. \qquad (13\text{-}200)$$

For the radial function given in Eq. (13-197) this condition implies

$$\tan \pi\nu + \tan \pi\mu_\ell = 0, \qquad (13\text{-}201)$$

where we have used Eqs. (13-198) and (13-199) together with the fact that the function $|C(r)\exp[r/(\nu a_0)]|$ does not go to zero as $r \to \infty$. Equation (13-201) can be rewritten as

$$\sin[\pi(\nu + \mu_\ell)] = 0, \qquad (13\text{-}202)$$

and has the solutions

$$\nu + \mu_\ell = n = 0, \pm 1, \pm 2, \pm 3, \ldots . \tag{13-203}$$

However, by analogy with the hydrogen atom we know that only the solutions

$$\nu + \mu_\ell = n = \ell + 1, \ell + 2, \ell + 3, \ldots \tag{13-204}$$

are physically meaningful. For these solutions we can use Eq. (13-193) to obtain

$$\epsilon = -\frac{E_h}{2(n - \mu_\ell)^2}; \quad n = \ell + 1, \ell + 2, \ell + 3, \ldots . \tag{13-205}$$

It turns out that the experimental energies of the Rydberg states in the sodium atom [with the core in its ground state] are well described by Eq. (13-205) if we set $\mu_\ell = -0.65$. The quantity ν is called the *effective quantum number*, and μ_ℓ, which measures the amount by which ν differs from an integer, is the *quantum defect*. The energies of the Rydberg states of the sodium atom are thus obtained without diagonalizing a matrix, and this theoretical technique is referred to as *Quantum Defect Theory* (QDT) [see Hartree (1928)].

An important generalization of QDT is *Multichannel Quantum Defect Theory* (MQDT). Ross (1991) discusses the application of MQDT to the determination of the electronic energies of the hydrogen molecule H_2. That is, MQDT is used to obtain the eigenvalues of $\hat{H}_{\text{elec}}$ [see Chapter 9] in an *ab initio*-type calculation. The calculations are carried out at fixed values of R, the distance between the two protons in H_2. The Born-Oppenheimer potential energy functions V_{N} of H_2, obtained essentially as the eigenvalues of $\hat{H}_{\text{elec}}$ taken as functions of R, show a complicated pattern with an infinite number of avoided crossings [see Fig. 8 of Ross (1991)], and it is the aim of the MQDT calculation to explain this pattern.

In MQDT the collision wavefunction is represented by an expression less restrictive than the *single channel* function in Eq. (13-196). In the present case, which we initially view as a collision between the Rydberg electron and the H_2^+ ion core with a fixed value of R, we make several channels available to the Rydberg electron. The channel wavefunctions are chosen as *diabatic* electronic wavefunctions. They can be thought of as a set of basis functions used for constructing a matrix representation for $\hat{H}_{\text{elec}}$. The eigenvalues of this matrix for a given value of R will be values of the Born-Oppenheimer potential energy functions V_{N}. As mentioned above these functions exhibit complicated avoided crossings as R varies. The avoided crossings are assumed to be caused by off-diagonal elements of the diabatic-basis matrix representation. The diagonal elements of this matrix, the *diabatic* energies, are taken to be smoothly varying functions of R that resemble the potential energy curves of isolated electronic states. In particular, the diabatic potential curves will cross where the Born-Oppenheimer ones have avoided crossings. The definition of diabatic electronic states given here is somewhat vague since the only requirement is that the quantum defect relating to such a series of diabatic states be a smoothly varying function of R. In practice one can often obtain a useful diabatic basis for a diatomic molecule by requiring the nuclear operator d/dR to be diagonal in this basis [Smith (1969)].

The channels are specified by the electronic state of the H_2^+ core and by the non-radial (angular) part of the Rydberg electron wavefunction. In the example discussed by Ross (1991) the H_2^+ core can occupy either its electronic ground state $\tilde{X}\,^2\Sigma_g^+$ or the first excited state $\tilde{A}\,^2\Sigma_u^+$ [see Figs. 17-8 and 17-9]. In the channels available to the Rydberg electron the two electronic states of H_2^+ can be combined with Rydberg electron functions of s [$\ell = 0$], p [$\ell = 1$], or d [$\ell = 2$] character; the Rydberg electron wavefunctions can also be labeled by their symmetries in $\boldsymbol{D}_{\infty h}$. We number the channels by a running index $i = 1, 2, 3, 4, \ldots, N_c$, and for each of them we introduce a wavefunction $|i\rangle$ analogous to the wavefunction $\Phi_{\rm core}^{(\ell)}(\boldsymbol{\omega})$ in Eq. (13-196), which describes the electronic state of the core and the non-radial part of the Rydberg electron wavefunction for this particular channel.

The quantity ν must be redefined relative to Eq. (13-193). In the present case the energy of the Rydberg electron is a function $\epsilon_i(R)$ of R given by the difference between the total Born-Oppenheimer electronic energy of the H_2 molecule, $V_{\rm N}(R)$, and the energy of the ion core for channel i, $V_{{\rm N},i}^+(R)$:

$$\epsilon_i(R) = V_{\rm N}(R) - V_{{\rm N},i}^+(R). \tag{13-206}$$

The ν value for channel i is thus

$$\nu_i(R) = \sqrt{-\frac{E_h}{2\epsilon_i(R)}}. \tag{13-207}$$

With this definition we express the complete wavefunction [analogous to the wavefunction in Eq. (13-196)] as

$$\Phi = \sum_{i=1}^{N_c} B_i \Phi_i, \tag{13-208}$$

where the expansion functions are

$$\Phi_i = f_{\ell_i}\Big(\nu_i(R), r\Big)\,|i\rangle - \sum_{j=1}^{N_c} K_{ij}(R)\, g_{\ell_j}\Big(\nu_j(R), r\Big)\,|j\rangle. \tag{13-209}$$

The square matrix $\mathbf{K}$ with elements $K_{ij}(R)$ is called the *reaction matrix*. Its dimension is the number of available channels N_c. It is easy to reorganize the function in Eq. (13-208) as

$$\Phi = \sum_{i=1}^{N_c} B_i \left[f_{\ell_i}\Big(\nu_i(R), r\Big) - \sum_{j=1}^{N_c} K_{ji}(R)\, g_{\ell_i}\Big(\nu_i(R), r\Big) \right] |i\rangle. \tag{13-210}$$

Obviously if the reaction matrix is diagonal with

$$K_{ij}(R) = \delta_{ij} \tan \pi\mu_{\ell_i}, \tag{13-211}$$

say, then Φ will be a linear combination of single-channel functions of the type obtained by inserting Eq. (13-197) in Eq. (13-196), and the theory would revert to Quantum Defect Theory. As explained by Ross (1991), in the MQDT calculation for H_2 discussed here the nonvanishing off-diagonal reaction matrix elements describe the interactions between the diabatic basis states which cause the avoided crossings present for the electronic states of H_2.

In order to determine the energies of the bound states of H_2 we require that $\epsilon < 0$ and that

$$\Phi \rightarrow 0 \text{ for } r \rightarrow \infty, \tag{13-212}$$

exactly as we did in the case of the Rydberg states of the sodium atom. By using Eqs. (13-198) and (13-199) it is straightforward to show that this condition will be satisfied if the determinant

$$|\tan[\pi\boldsymbol{\nu}] + \mathbf{K}| = 0. \tag{13-213}$$

Here, $\tan[\pi\boldsymbol{\nu}]$ is an $N_c \times N_c$ diagonal matrix with the diagonal elements

$$(\tan[\pi\boldsymbol{\nu}])_{ii} = \tan[\pi\nu_i(R)]. \tag{13-214}$$

With the definition

$$\mu_{ij}(R) = \frac{1}{\pi} \tan^{-1} K_{ij}(R) \tag{13-215}$$

[cf. Eq. (13-211)] we can rewrite Eq. (13-213) as

$$|\tan[\pi\boldsymbol{\nu}] + \tan[\pi\boldsymbol{\mu}]| = 0, \tag{13-216}$$

where $(\tan[\pi\boldsymbol{\mu}])_{ij} = \tan[\pi\mu_{ij}(R)]$. The matrix $\boldsymbol{\mu}(R)$ with elements $\mu_{ij}(R)$ is the *quantum defect matrix*. We note the similarity between Eqs. (13-216) and (13-201). If the quantum defect matrix and the ion core energies $V^{+}_{\mathrm{N},i}(R)$ are known, then the bound state electronic energies $V_{\mathrm{N}}(R)$ can be obtained by solving Eq. (13-216). These energies enter into the equation through the ν_i's defined by Eqs. (13-206) and (13-207). It is not immediately clear, however, how to obtain the quantum defect matrix $\boldsymbol{\mu}(R)$. Ross and Jungen (1987) have developed a method of fitting the quantum defect matrix to the *ab initio* potential curves for H_2 and were able to calculate the Born-Oppenheimer potential curves with high accuracy.

It should be noted that the *electronic* MQDT calculation is simplified by molecular symmetry. In the present case of the electronic energies of H_2, the wavefunction Φ in Eq. (13-208) must necessarily transform according to one of the irreducible representations of the molecular point group $\boldsymbol{D}_{\infty\mathrm{h}}$. If the expansion functions Φ_i in Eq. (13-208) are symmetrized in this group, the quantum defect matrix $\boldsymbol{\mu}(R)$ will be block diagonal with each block corresponding to an irreducible representation in $\boldsymbol{D}_{\infty h}$. Thus, Eq. (13-214) can be solved independently for each of the irreducible representations in the point group, in much the same way as the diagonalization of the matrix representation of a Hamiltonian can be separated into independent diagonalizations, one for each of the irreducible representations in the symmetry group for the Hamiltonian in question. For example, Ross (1991) discusses two separate electronic MQDT calculations: one to determine the potential curves of the $^1\Pi_u$ electronic states of H_2, and another to determine the potential curves of the $^1\Sigma_g^+$ states.

We have outlined MQDT for the purpose of calculating all the series of Rydberg electronic state potential energy curves and wavefunctions as a function of the internuclear separation for the hydrogen molecule. The ideas outlined here turn out to be extremely powerful, and it is possible to extend them to other molecules and to develop vibronic and rovibronic MQDT. Incorporating vibration and rotation naturally results in the inclusion of the bulk of the adiabatic and non-adiabatic effects in one fell swoop. Extended above threshold the MQDT wavefunctions account for couplings with continua (and between continua) allowing the calculation of the effects of autoionization and predissociation, and of the effect of the competition between these processes. Stark and Zeeman effects can also be incorporated into the MQDT treatment. All of this is within the same general formulation and possible from the same fundamental quantities: the elements of $\boldsymbol{\mu}(R)$. The reader is referred to Molecular Applications of Quantum Defect Theory (1996) for a compilation of important papers on MQDT and related methods; this publication also includes an extraordinarily extensive bibliography.

13.6 SPIN EFFECTS

Notation: Up to now in this chapter, and elsewhere in the book when we consider singlet states ($S = 0$), we have followed accepted singlet-state convention of using J, rather than the N, as the rovibronic angular momentum quantum number. Since we wish the equations developed in the remainder of the chapter to be applicable to states of any multiplicity we now use the consistent notation introduced in Section 10.3.3. It is useful to summarize that notation here.

The total angular momentum is denoted $\hat{\boldsymbol{F}}$ and it is given by Eq. (10-99). The operators $\hat{\boldsymbol{N}}^2$, $\hat{N}_z$, and $\hat{N}_\zeta$, where the two latter operators are the components of $\hat{\boldsymbol{N}}$ along the molecule fixed z axis and the space fixed ζ axis, respectively, represent the rovibronic angular momentum. In the remainder of the present chapter, we use the consistent notation that $\hat{\boldsymbol{J}}$ denotes $\hat{\boldsymbol{N}} + \hat{\boldsymbol{S}}$ [Eq. (10-97)], and we generally consider states with $S > 0$ for which $\hat{\boldsymbol{J}} \neq \hat{\boldsymbol{N}}$. The simultaneous eigenfunctions for $\hat{\boldsymbol{N}}^2$, $\hat{N}_z$, and $\hat{N}_\zeta$ are the symmetric top functions $|N, k, m\rangle$ obtained from Eq. (11-52) by setting $J = N$, and the eigenvalues are obtained from Table 11-1 as $N(N+1)\hbar^2$, $k\hbar$, and $m\hbar$, respectively. The quantum numbers associated with the various operators are such that [see Eqs. (10-95) and (10-96)]

- $\hat{\boldsymbol{S}}^2$ and $\hat{S}_\zeta$ have the eigenvalues $S(S+1)\hbar^2$ and $m_S\hbar$, respectively,
- $\hat{\boldsymbol{J}}^2$ and $\hat{J}_\zeta$ have the eigenvalues $J(J+1)\hbar^2$ and $m_J\hbar$, respectively, and
- $\hat{\boldsymbol{I}}^2$ and $\hat{I}_\zeta$ have the eigenvalues $I(I+1)\hbar^2$ and $m_I\hbar$, respectively.

Since $\hat{\boldsymbol{J}} = \hat{\boldsymbol{N}} + \hat{\boldsymbol{S}}$, the possible values for J are $|N-S|, |N-S|+1, \ldots, N+S$, and since $\hat{\boldsymbol{F}} = \hat{\boldsymbol{J}} + \hat{\boldsymbol{I}}$, the possible values for F are $|J-I|, |J-I|+1, \ldots, J+I$. The quantum numbers S, J, I, and F [and thus m_S, m_J, m_I, and m_F] can be half-integral.

The spin-free Hamiltonian: Up to now in the present chapter, we have neglected the spin-dependent contributions $\hat{H}_{\mathrm{es}}$ [see Eqs. (7-20)-(7-22)] and $\hat{H}_{\mathrm{hfs}}$ [Eq. (7-23)] to the molecular Hamiltonian, and have taken the Hamiltonian to be given entirely by the rovibronic Hamiltonian $\hat{H}_{\mathrm{rve}}$ from Eq. (7-33). In the absence of spin effects, we can express the internal wavefunctions as

$$\begin{aligned}\Phi_{\mathrm{int}}^{(N,m,S,m_S,I,m_I)} &= \Phi_{\mathrm{nspin}}^{(I,m_I)} \sum_{e,V,L,k} c_{eVLk}^{(N)}\, \Phi_{\mathrm{elec}}^{(e,S,m_S)}\, \Phi_{\mathrm{rv}}^{(V,L,N,k,m)} \\ &= \Phi_{\mathrm{nspin}}^{(I,m_I)} \sum_{e,V,L,k} c_{eVLk}^{(N)}\, \Phi_{\mathrm{elec}}^{(e,S,m_S)}\, \Phi_{\mathrm{vib}}^{(V,L)}\, |N,k,m\rangle\,, \qquad (13\text{-}217)\end{aligned}$$

where $\Phi_{\mathrm{rv}}^{(V,L,N,k,m)}$ is a rotation-vibration basis function defined by Eq. (12-73) [with the substitution $J \to N$ explained above], and the function $\Phi_{\mathrm{vib}}^{(V,L)}$ is the product of harmonic oscillator functions contained in $\Phi_{\mathrm{rv}}^{(V,L,N,k,m)}$. We use these basis functions also for asymmetric top molecules, bearing in mind that they have no l quantum numbers so that in this case, we can ignore the label L. The expansion coefficients $c_{eVLk}^{(N)}$ in Eq. (13-217) have been obtained by diagonalizing a matrix representation of $\hat{H}_{\mathrm{rve}}$ in a basis of $\Phi_{\mathrm{elec}}^{(e,S,m_S)}\, \Phi_{\mathrm{rv}}^{(V,L,N,k,m)}$ functions. The summation over electronic state e in Eq. (13-217) will be necessary if vibronic or rovibronic interactions are present. Even though we neglect all spin contributions to the molecular Hamiltonian here we retain the nuclear spin function $\Phi_{\mathrm{nspin}}^{(I,m_I)}$ [which we can choose as a simultaneous eigenfunction for $\hat{\boldsymbol{I}}^2$ and $\hat{I}_\zeta$ with the eigenvalues given above], and the electron spin functions present in $\Phi_{\mathrm{elec}}^{(e,S,m_S)}$ [see Chapter 9] in order to ensure that the $\Phi_{\mathrm{int}}^{(N,m,S,m_S,I,m_I)}$ comply with the Pauli exclusion principle [see page 139].

As indicated in Eq. (13-217), we can label the internal wavefunction by the quantum numbers N, m, S, m_S, I, and m_I. They are all good quantum numbers because the spin-free molecular Hamiltonian $\hat{H}_{\mathrm{rve}}$ commutes with the operators $\hat{\boldsymbol{N}}^2$, $\hat{N}_\zeta$, $\hat{\boldsymbol{S}}^2$, $\hat{S}_\zeta$, $\hat{\boldsymbol{I}}^2$, and $\hat{I}_\zeta$ associated with them.

Electron spin: For electronic states with $S > 0$ it is necessary to take into account the electron-spin dependent contributions to the molecular Hamiltonian. That is, we take the Hamiltonian to be

$$\hat{H}_{\mathrm{rves}} = \hat{H}_{\mathrm{rve}} + \hat{H}_{\mathrm{es}}, \qquad (13\text{-}218)$$

where the various contributions to $\hat{H}_{\rm es}$ are given by Eqs. (7-20)-(7-22). The Hamiltonian $\hat{H}_{\rm rves}$ commutes with $\hat{\boldsymbol{J}}^2$ and $\hat{J}_\zeta$ and with $\hat{\boldsymbol{I}}^2$ and $\hat{I}_\zeta$, but it does *not* commute with $\hat{\boldsymbol{N}}^2$, $\hat{N}_\zeta$, $\hat{\boldsymbol{S}}^2$, and $\hat{S}_\zeta$. Hence J, m_J, I, and m_I are now good quantum numbers, whereas N, m, S, and m_S are not. They are, at best, near quantum numbers. We use a basis of eigenfunctions for $\hat{\boldsymbol{J}}^2$ and $\hat{J}_\zeta$ to construct a matrix representation of $\hat{H}_{\rm rves}$ that we can diagonalize to obtain the energies and wavefunctions. If the energy contributions resulting from the nonzero electron spin are small, we can use a Hund's case (b) basis, and the internal wavefunction will be given as

$$\Phi_{\rm int}^{(J,m_J,I,m_I)} = \Phi_{\rm nspin}^{(I,m_I)} \sum_{e,V,L,N,S,k} c_{eVLNSk}^{(J)}\, \Phi_{\rm vib}^{(V,L)}\, \Phi_{\rm er}^{(e,N,S,J,k,m_J)}. \tag{13-219}$$

The electronic-rotational basis functions in Eq. (13-219) are obtained from Eq. (10-98):

$$\Phi_{\rm er}^{(e,N,S,J,k,m_J)} = \sum_{m=-N}^{N} \sum_{m_S=-S}^{S} (-1)^{N-S+m_J}\sqrt{2J+1} \times \begin{pmatrix} N & S & J \\ m & m_S & -m_J \end{pmatrix} \left|\Phi_{\rm elec}^{(e,S,m_S)}\right\rangle |N,k,m\rangle . \tag{13-220}$$

Nuclear spin: Finally, we take into account the nuclear hyperfine term $\hat{H}_{\rm hfs}$ [Eq. (7-23)], so that we now employ the complete internal Hamiltonian $\hat{H}_{\rm int}$ from Eq. (7-28). This Hamiltonian commutes with $\hat{\boldsymbol{F}}^2$ and $\hat{F}_\zeta$, but *not* with $\hat{\boldsymbol{J}}^2$, $\hat{J}_\zeta$, $\hat{\boldsymbol{S}}^2$, $\hat{S}_\zeta$, $\hat{\boldsymbol{I}}^2$, or $\hat{I}_\zeta$. The eigenfunctions of $\hat{H}_{\rm int}$ are written as

$$\Phi_{\rm int}^{(F,m_F)} = \sum_{e,V,L,S,I} \sum_{J=|F-I|}^{F+I} \sum_{N=|J-S|}^{J+S} \sum_{k=-N}^{N} c_{eVLIJSNk}^{(F)}\, \Phi_{\rm vib}^{(V,L)}\, \Phi_{\rm erns}^{(e,F,I,N,J,S,k,m_F)}, \tag{13-221}$$

where

$$\Phi_{\rm erns}^{(e,F,I,N,J,S,k,m_F)} = \sum_{m_J=-J}^{J} \sum_{m_I=-I}^{I} (-1)^{J-I+m_F}\sqrt{2F+1} \times \begin{pmatrix} J & I & F \\ m_J & m_I & -m_F \end{pmatrix} \Phi_{\rm nspin}^{(I,m_I)} \Phi_{\rm er}^{(e,N,S,J,k,m_J)}. \tag{13-222}$$

In Eqs. (13-217), (13-219), and (13-221) we have sketched the "development" of the internal wavefunction as we consider first the effects of electron spin, and then the effects of nuclear spin, in the molecular Hamiltonian. The crudest approximation for the internal wavefunction is the completely separable wavefunction in Eq. (13-1) for which e, V, L, N, k, m, S, m_S, J, m_J, I, m_I, F, and m_F are all good quantum numbers. Vibronic and rovibronic interactions spoil e [and possibly also V, L, and k], rotation-vibration interaction spoils

V, L, and k, electron spin effects spoil N, m, S, and m_S, and nuclear spin effects spoil J, m_J, I, and m_I. When a quantum number loses its status as a good quantum number, it becomes a basis function label and appears as a summation index in the expression giving the wavefunction in terms of the appropriate basis functions. We can use successively less approximate expressions for the wavefunction, and spoil successively more quantum numbers, until we reach the final expression for the wavefunction in Eq. (13-221). For an isolated molecule in field free space, the good quantum numbers F and m_F in this equation cannot be spoiled since they are determined by the symmetry of the wavefunction in $\boldsymbol{K}$(spatial). Also, the operations of the MS group commute with all terms in the internal Hamiltonian, and so the irreducible representation of the wavefunction in the MS group is also a "good quantum number" [in the sense that it can be used to label the internal wavefunction] regardless of the approximation employed for the molecular Hamiltonian. In the presence of external electric and magnetic fields the quantum numbers (F, m_F), and the MS group symmetry with respect to P^* operations, can be spoiled. This is discussed in Chapter 14.

The remainder of the present section is concerned with the symmetries of the basis functions entering into Eqs. (13-217), (13-219), and (13-221), and with some of the more important contributions to $\hat{H}_{es}$ and $\hat{H}_{hfs}$. The theory of spin effects is an extensive topic and we focus on the symmetry aspects. Since we consider here non-linear molecules [linear molecules are the subject of Chapter 17], for which the spin coupling is generally close to Hund's case (b), our treatment is limited to the Hund's case (b) basis functions given in Eq. (13-219). Equation (23a) of Brown and Howard (1976) gives the transformation between Hund's case (a) and Hund's case (b) basis functions.

13.6.1 Electron spin effects

It follows from Eqs. (12-46) and (12-47) that all the $|N, k, m\rangle$ functions, for given N and k, used in Eq. (13-220) to form a bsis function $\Phi_{\rm er}$ have the same symmetry in the MS group [i.e., this symmetry does not depend on m]; similarly the MS group symmetry of $\Phi_{\rm elec}^{(e,S,m_S)}$ is independent of m_S [see Chapter 12]. Because the basis function $\Phi_{\rm er}^{(e,N,S,J,k,m_J)}$ has the same MS group symmetry as any one of the products $\Phi_{\rm elec}^{(e,S,m_S)}\,|N, k, m\rangle$ on the right hand side of Eq. (13-220) each of the products $\Phi_{\rm vib}^{(V,L)}\Phi_{\rm er}^{(e,N,S,J,k,m_J)}$ in Eq. (13-219) has the MS group symmetry $\Gamma_{\rm rve}$. In $\boldsymbol{K}$(spatial), the wavefunctions in Eq. (13-219) transform according to the irreducible representation $D^{(J)}$.

The most important contribution to $\hat{H}_{es}$ is the electron spin–orbit interaction term given by Eq. (7-20). The nonvanishing matrix elements of this operator between the basis functions $\Phi_{\rm er}^{(e,N,S,J,k,m_J)}$ can be shown to have

$$|\Delta S| \leq 1 \tag{13-223}$$

[see, for example, Section 5.4 of Zare (1988)]. Thus, electron spin–orbit interaction can couple the rovibronic basis states of a singlet state [$S = 0$] with those of a triplet state [$S = 1$]. The methylene radical CH_2 provides an example of such *singlet-triplet interaction*. The bending potential energy curves for the lowest three electronic states of CH_2 are shown in Fig. 13-14. The singlet curves are from Jensen and Brumm (1996) and the triplet curve is from Jensen and Bunker (1988). The electronic ground state is $\tilde{X}\,{}^3B_1$, and there are two low-lying singlet states $\tilde{a}\,{}^1A_1$ and $\tilde{b}\,{}^1B_1$. As we have already discussed in connection with Fig. 13-7, the latter two states are subject to the Renner effect; they are degenerate as a ${}^1\Delta_g$ state at linearity. It has been shown experimentally that several rotational states in the $\tilde{a}\,{}^1A_1$ vibrational ground state are significantly mixed with rovibrationally excited states of the $\tilde{X}\,{}^3B_1$ electronic ground state. The identification of these perturbations, in conjunction with an *ab initio* calculation of the spin–orbit interaction matrix elements responsible for them, allowed an accurate determination of the *singlet-triplet splitting* [i.e., the energy difference between the $\tilde{a}$ and $\tilde{X}$ vibrational ground states in CH_2]; see McKellar, Bunker, Sears, Evenson, Saykally, and Langhoff (1983) [henceforth: MBSESL] and Jensen and Bunker (1988). The singlet-triplet interaction in CH_2 plays an important role in the collision-induced "intersystem crossing", i.e., the reaction

$$CH_2(\tilde{a}\,{}^1A_1) + M \rightarrow CH_2(\tilde{X}\,{}^3B_1) + M,$$

where M is a collision partner; see Bley and Temps (1993).

MBSESL determined the singlet-triplet interaction matrix elements for CH_2 by calculating the purely electronic integrals

$$H_{\mathrm{SO}}^{(\tilde{X}\tilde{a})}(m_S) = \left\langle \Phi_{\mathrm{elec}}^{(\tilde{X},1,m_S)} \middle| \hat{H}_{\mathrm{so}} + \hat{H}_{\mathrm{sr}} \middle| \Phi_{\mathrm{elec}}^{(\tilde{a},0,0)} \right\rangle \tag{13-224}$$

of the operators $\hat{H}_{\mathrm{so}}$ and $\hat{H}_{\mathrm{sr}}$ [Eqs. (7-20) and (7-21)] in *ab initio* calculations. By neglecting the small nuclear-velocity term $\boldsymbol{P}_\alpha/m_\alpha$ in Eq. (7-21) they could express the quantity $H_{\mathrm{SO}}^{(\tilde{X}\tilde{a})}(m_S)$ as a function of the nuclear coordinates only. This function was computed at a number of different nuclear geometries, obtained by varying the bond angle supplement $\rho = \pi - \angle(\mathrm{HCH})$ of CH_2 for constant bond lengths, and the resulting values were fitted to a parameterized function of ρ [Eq. (10) of MBSESL]. As demonstrated by MBSESL, at least in principle, it is straightforward to use $H_{\mathrm{SO}}^{(\tilde{X}\tilde{a})}(m_S)$ for obtaining the matrix elements between the basis functions $\Phi_{\mathrm{vib}}^{(V_X,L_X)}\,\Phi_{\mathrm{er}}^{(\tilde{X},N_X,S_X,J_X,k_X,m_J)}$ [Eq. (13-219)] for the triplet $\tilde{X}$ state and $\Phi_{\mathrm{elec}}^{(\tilde{a},0,0)}\,\Phi_{\mathrm{vib}}^{(V_a,L_a)}\,|N_a,k_a,m\rangle$ [Eq. (13-217)] for the singlet $\tilde{a}$ state. In practice, the integrations over the rotational and vibrational coordinates may cause some difficulty because of *axis switching* effects [see page 434 below]. Such effects were neglected by MBSESL.

The "microscopic" expressions for $\hat{H}_{\mathrm{so}}$ and $\hat{H}_{\mathrm{sr}}$ [involving the angular momenta and spins of the individual electrons and nuclei] given in Eqs. (7-20) and (7-21) are only useful for *ab initio* calculations such as the one carried out by MBSESL. If spin–orbit coupling is to be taken into account in a fitting to

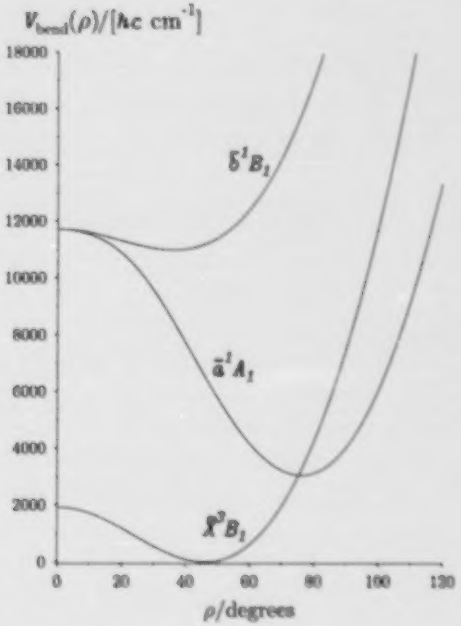

Fig. 13-14. Bending potential curves for the lowest electronic states of the methylene radical CH_2. The abscissa is the bending coordinate $\rho = \pi - \angle(\mathrm{HCH})$, the supplement of the bond angle. The bond lengths are held constant.

experimentally observed transition wavenumbers, it is necessary to introduce simpler, parameterized forms of the spin–orbit coupling operator. If we neglect spin–orbit matrix elements with $\Delta S \neq 0$, we can replace the microscopic form of the spin–orbit coupling operator by

$$\hat{H}_{\mathrm{SO}} = A_{\mathrm{SO}}\, \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} \tag{13-225}$$

where $\hat{\boldsymbol{L}}$ is the electronic angular momentum vector, and A_{SO} is an adjustable parameter [see, for example, Van Vleck (1951), Condon and Shortley (1953) and Landau and Lifshitz (1977)]. This phenomenological form of the spin–orbit coupling operator is used to describe the interaction between different electronic states of the same multiplicity. Hallin and Merer (1977) propose a spin–orbit coupling operator of the form

$$\hat{H}_{\mathrm{SO}} = \sum_{\gamma,\delta=x,y,z} A_{\gamma\delta}\, \hat{L}_\gamma \hat{S}_\delta, \tag{13-226}$$

where the sum runs over the molecule fixed axes x, y, and z and the $A_{\gamma\delta}$ are spin–orbit coupling coefficients. They derive the matrix elements of this operator between the basis functions given by Eq. (13-219). The nonvanishing matrix elements satisfy

$$\Delta S = 0, \ \ |\Delta N| \leq 1, \text{ and } |\Delta k| \leq 1. \tag{13-227}$$

From the matrix elements of Hallin and Merer (1977), we can also obtain the matrix elements of the operator in Eq. (13-225) by simply setting $A_{xx} = A_{yy} = A_{zz} = A_{\mathrm{SO}}$ and $A_{\gamma\delta} = 0$ for $\gamma \neq \delta$.

If we are concerned with one electronic state having $S > 0$, and this electronic state is well separated in energy from all other electronic states, we can use the contact transformation procedure[13] to eliminate the spin–orbit matrix elements coupling the electronic state under study with other electronic states. Van Vleck (1951) has shown that by applying this procedure to the combined effects of spin–orbit coupling and the term $\hat{T}_{\mathrm{er}}$ in Eq. (13-143), one obtains a contribution to the effective spin-rotation Hamiltonian

$$\hat{H}_{\mathrm{sr}} = \frac{1}{2} \sum_{\gamma\delta=x,y,z} \epsilon_{\gamma\delta} \left(\hat{N}_\gamma \, \hat{S}_\delta + \hat{S}_\gamma \hat{N}_\delta\right) \tag{13-228}$$

where $\epsilon_{\gamma\delta}$ is an element of the spin-rotation tensor. Another contribution to $\hat{H}_{\mathrm{sr}}$ involves the direct interaction between the spin magnetic moments of the electrons and the magnetic moment resulting from the nuclear motion. Brown, Sears, and Watson (1980) give a detailed derivation of $\hat{H}_{\mathrm{sr}}$, starting with the microscopic form of the spin–orbit coupling operator [see Barnes, Brown, Carrington, Pinkstone, Sears, and Thistlethwaite (1978) for a simpler derivation starting with the operator in Eq. (13-225)]. The operator $\hat{H}_{\mathrm{sr}}$ describes the effects of spin–orbit coupling within the one electronic state under study; the coupling of this state to other electronic states need not be explicitly considered. The matrix elements of $\hat{H}_{\mathrm{sr}}$ between the basis functions given by Eq. (13-219) can be obtained from the paper by Bowater, Brown, and Carrington (1973)[14]. The nonvanishing matrix elements satisfy

$$\Delta S = 0, \ \ |\Delta N| \leq 1, \text{ and } |\Delta k| \leq 2. \tag{13-229}$$

Brown and Sears (1979) have used the contact transformation technique to obtain $\hat{H}_{\mathrm{sr}}$ in a form suitable for fitting to observed energies.

For one isolated electronic state with $S > 0$ the electron spin-spin interaction [Eq. (7-22)] is usually taken to be described by the effective operator [Van Vleck (1951); see also Raynes (1964)]

$$\hat{H}_{\mathrm{ss}} = \frac{D}{3} \left[2\hat{S}_a^2 - \hat{S}_b^2 - \hat{S}_c^2\right] + E \left[\hat{S}_b^2 - \hat{S}_c^2\right] \tag{13-230}$$

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[13] See Section 13.2.4 and the discussion on page 364.

[14] See also Eq. (20) of Kosin and Jensen (1997), but note that this reference has a factor $i^{k-k'}$ which results from a phase choice for the rotational functions different from that made in this book. Matrix elements appropriate for the phase choice made here are obtained by omitting this factor.

where D and E are parameters and $\left(\hat{S}_a, \hat{S}_b, \hat{S}_c\right)$ are the components of the total electron spin along the a, b and c principal molecule fixed axes defined in the discussion below Fig. 10-2 on page 210. The abc axes must be correlated with the molecule fixed axes xyz for the molecule in question. The parameters D and E are related to the parameters α and β of Van Vleck (1951) by $D = 3\alpha$ and $E = \beta$. The nonvanishing matrix elements of $\hat{H}_{ss}$ have

$$\Delta S = 0, \ |\Delta N| \leq 2, \text{ and } |\Delta k| \leq 2; \tag{13-231}$$

they can be obtained from Eq. (22) of Kozin and Jensen (1997)[15].

For the nonlinear molecules considered here, N will normally be a near quantum number. The effect of $\hat{H}_{es}$ will be to make a rovibronic energy level [i.e., an eigenstate of H_{rve}] split into $2S + 1$ fine structure components,[16] each one characterized by a value of $J = |N - S|, |N - S| + 1, \ldots, N + S$. In a doublet state the level with $J = N + \frac{1}{2}$ is called the F_1 fine structure component, and the level with $J = N - \frac{1}{2}$ is called the F_2 component. In a triplet state the levels with $J = N + 1$, N and $N - 1$ are called the F_1, F_2 and F_3 components, respectively. The energy splittings between these components will be small compared to a typical rotational energy level difference. It follows from the discussion above that the nuclear-spin-free wavefunctions [i.e., the function multiplied by $\Phi_{\rm nspin}^{(I,m_I)}$ on the right hand side of Eq. (13-219)] of all the J components, for a given N, will have the same MS group symmetry $\Gamma_{\rm rve}$.

13.6.2 Nuclear spin effects

The internal wavefunction $\Phi_{\rm int}$ in Eq. (13-221) must necessarily transform in the MS group according to one of the two irreducible representations $\Gamma_{\rm MS}^{+}$ and $\Gamma_{\rm MS}^{-}$ allowed by the Pauli exclusion principle [see Chapter 8]. As discussed in Chapter 7, $\Phi_{\rm int}$ transforms in $\boldsymbol{K}$(spatial) according to the row labeled m_F in the irreducible representation $D^{(F)}$. In this subsection and the next (on ortho-para conversion) we continue to use N as the rovibronic angular momentum quantum number for generality. For singlet states it is (unfortunately) the custom to use J.

The MS group symmetry of the function $\Phi_{\rm erns}^{(e,F,I,N,J,S,k,m_F)}$ in Eq. (13-221) depends on the symmetries of the $\Phi_{\rm er}^{(e,N,S,J,k,m_J)}$ functions [see above], and on the symmetries of the nuclear spin functions $\Phi_{\rm nspin}^{(I,m_I)}$. In order to determine these latter symmetries, we must consider the detailed form of the $\Phi_{\rm nspin}^{(I,m_I)}$ functions. As an example, we consider the spin functions for the three protons in NH_3 [MS group $\boldsymbol{D}_{3h}$(M); see Table A-10] defined in Eq. (8-4).

For each of the three protons [labeled with the index $\alpha = 1, 2$, or 3] in $^{14}NH_3$ there are spin operators $\hat{\boldsymbol{I}}_\alpha{}^2$ and $\hat{I}_{\zeta,\alpha}$ with associated eigenfunctions $|I_\alpha, m_{I_\alpha}\rangle$

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[15] **Where once again it should be noted that in order to obtain matrix elements consistent with the phase choices made here, the factor of $i^{k-k'}$ in the expression by Kozin and Jensen (1997) should be omitted.**

[16] **There will be fewer components if $N < S$.**

where the quantum numbers $I_\alpha = 1/2$ and $m_{I_\alpha} = -1/2$ or $1/2$. We couple the spins of protons 1 and 2 to form the operators

$$\hat{\boldsymbol{I}}_{1-2}{}^2 = \left(\hat{\boldsymbol{I}}_1 + \hat{\boldsymbol{I}}_2\right)^2 \tag{13-232}$$

and

$$\hat{I}_{\zeta,1-2} = \hat{I}_{\zeta,1} + \hat{I}_{\zeta,2}. \tag{13-233}$$

These operators have the eigenvalues $I_{1-2}(I_{1-2}+1)\hbar^2$ and $m_{I,1-2}\hbar$, and the corresponding eigenfunctions $|I_{1-2}, m_{I,1-2}\rangle$ can be obtained as linear combinations of the products $|I_1, m_{I_1}\rangle\,|I_2, m_{I_2}\rangle$ by using Eq. (10-98). The possible values for I_{1-2} are 0 and 1. We define

$$\hat{\boldsymbol{I}}_{1-3}{}^2 = \left(\hat{\boldsymbol{I}}_1 + \hat{\boldsymbol{I}}_2 + \hat{\boldsymbol{I}}_3\right)^2 = \left(\hat{\boldsymbol{I}}_{1-2} + \hat{\boldsymbol{I}}_3\right)^2 \tag{13-234}$$

and

$$\hat{I}_{\zeta,1-3} = \hat{I}_{\zeta,1} + \hat{I}_{\zeta,2} + \hat{I}_{\zeta,3} = \hat{I}_{\zeta,1-2} + \hat{I}_{\zeta,3}. \tag{13-235}$$

The quantum numbers associated with $\hat{\boldsymbol{I}}_{1-3}{}^2$ and $\hat{I}_{\zeta,1-3}$ are I_{1-3} and $m_{I,1-3}$, respectively, and we can obviously use Eq. (10-98) again to obtain the corresponding eigenfunctions. If $I_{1-2} = 0$, then the only possible value for I_{1-3} is 1/2, but if $I_{1-2} = 1$, I_{1-3} can assume the values 1/2 and 3/2. The ^{14}N nucleus in ^{14}NH$_3$ [labeled 4] has $I_4 = 1$. We form the two operators

$$\hat{\boldsymbol{I}}^2 = \left(\hat{\boldsymbol{I}}_1 + \hat{\boldsymbol{I}}_2 + \hat{\boldsymbol{I}}_3 + \hat{\boldsymbol{I}}_4\right)^2 = \left(\hat{\boldsymbol{I}}_{1-3} + \hat{\boldsymbol{I}}_4\right)^2 \tag{13-236}$$

and

$$\hat{I}_\zeta = \hat{I}_{\zeta,1} + \hat{I}_{\zeta,2} + \hat{I}_{\zeta,3} + \hat{I}_{\zeta,4} = \hat{I}_{\zeta,1-3} + \hat{I}_{\zeta,4} \tag{13-237}$$

with associated quantum numbers I and m_I, respectively. If $I_{1-3} = 1/2$, then the possible values of I are 1/2 and 3/2, and if $I_{1-3} = 3/2$, then the possible values of I are 1/2, 3/2, and 5/2. The eigenfunctions of $\hat{\boldsymbol{I}}^2$ and $\hat{I}_\zeta$, $|I, m_I\rangle$ can be determined from Eq. (10-98) in terms of the products $|I_{1-3}, m_{I,1-3}\rangle\,|I_4, m_{I_4}\rangle$. By inserting successively $|I_{1-3}, m_{I,1-3}\rangle$ in terms of $|I_{1-2}, m_{I,1-2}\rangle\,|I_3, m_{I_3}\rangle$ and $|I_{1-2}, m_{I,1-2}\rangle$ in terms of $|I_1, m_{I_1}\rangle\,|I_2, m_{I_2}\rangle$, we finally obtain expressions for $|I, m_I\rangle$ in terms of the products $|I_1, m_{I_1}\rangle\,|I_2, m_{I_2}\rangle\,|I_3, m_{I_3}\rangle\,|I_4, m_{I_4}\rangle$. The transformation properties of such products in the MS group are easily determined [see Chapter 8], and thus we can determine the MS group symmetries of the $|I, m_I\rangle$ functions.

It is clear from the preceding discussion that the quantum numbers I and m_I do not uniquely label an eigenfunction of $\hat{\boldsymbol{I}}^2$ and $\hat{I}_\zeta$. In the case of ^{14}NH$_3$, uniquely labeled functions would be $|I_{1-2}, I_{1-3}; I, m_I\rangle$, and the following functions exist: $|0, 1/2; 1/2, m_I\rangle$, $|0, 1/2; 3/2, m_I\rangle$, $|1, 1/2; 1/2, m_I\rangle$, $|1, 1/2; 3/2, m_I\rangle$, $|1, 3/2; 1/2, m_I\rangle$, $|1, 3/2; 3/2, m_I\rangle$, and $|1, 3/2; 5/2, m_I\rangle$, where, for each set of functions, $m_I = -I, -I+1, \ldots, I$.

We can generalize the somewhat cumbersome considerations here to the case of N nuclei. We use the following *coupling scheme*

$$\hat{\boldsymbol{I}}_1 + \hat{\boldsymbol{I}}_2 = \hat{\boldsymbol{I}}_{1-2} \qquad (13\text{-}238)$$

$$\hat{\boldsymbol{I}}_{1-2} + \hat{\boldsymbol{I}}_3 = \hat{\boldsymbol{I}}_{1-3} \qquad (13\text{-}239)$$

$$\hat{\boldsymbol{I}}_{1-3} + \hat{\boldsymbol{I}}_4 = \hat{\boldsymbol{I}}_{1-4} \qquad (13\text{-}240)$$

$$\vdots$$

$$\hat{\boldsymbol{I}}_{1-(N-1)} + \hat{\boldsymbol{I}}_N = \hat{\boldsymbol{I}}. \qquad (13\text{-}241)$$

$$\hat{\boldsymbol{I}} + \hat{\boldsymbol{J}} = \hat{\boldsymbol{F}}. \qquad (13\text{-}242)$$

Each of the operators $\hat{\boldsymbol{I}}_{1-\alpha}{}^2$, $\alpha = 2, 3, \ldots, N-1$, has an associated quantum number $I_{1-\alpha}$, and the labels $|I_{1-2}, I_{1-3}, \ldots, I_{1-(N-1)}; I, m_I\rangle$ uniquely define an eigenfunction of $\hat{\boldsymbol{I}}^2$ and $\hat{I}_\zeta$. We use $|\mathcal{I}; I, m_I\rangle$ as a shorthand notation where the label $\mathcal{I}$ represents all the "intermediate" I quantum numbers. The coupling scheme given by Eqs. (13-238)-(13-242) is the 'Equal or Nearly Equal Coupling Representation' employed by Cook and De Lucia (1971). Other coupling schemes are, of course, possible [see, for example, Cook and De Lucia (1971) and Thaddeus, Krisher, and Loubser (1964)].

We do not always have to derive the detailed form of the $|\mathcal{I}; I, m_I\rangle$ functions to determine their symmetries in the MS group. We again use the $^{14}NH_3$ molecule as example. Initially, we ignore the ^{14}N nucleus. We are only concerned with the spin functions for the three protons which we label $|I_{1-2}; I_{1-3}, m_{I,1-3}\rangle$ as described above. In connection with Eq. (8-4), we have already discussed the symmetries of the products $|I_1, m_{I_1}\rangle\,|I_2, m_{I_2}\rangle\,|I_3, m_{I_3}\rangle$, and it is immediately obvious that

$$|I_{1-2}; I_{1-3}, m_{I,1-3}\rangle = |1; 3/2, \;\; 3/2\rangle = \Phi_{\rm ns}^{(1)}$$

and

$$|1; 3/2, -3/2\rangle = \Phi_{\rm ns}^{(8)},$$

where $\Phi_{\rm ns}^{(1)}$ and $\Phi_{\rm ns}^{(8)}$ are defined in Eq. (8-4). These two functions both have A_1' symmetry in $\boldsymbol{D}_{3h}(\mathrm{M})$.

The space fixed components $(\hat{I}_{\xi,1-3}, \hat{I}_{\eta,1-3}, \hat{I}_{\zeta,1-3})$ of the total proton spin $\hat{\boldsymbol{I}}_{1-3}$ obey commutation relations analogous to those given in Eq. (10-90) for the space fixed components of $\hat{\boldsymbol{J}}$; the space fixed components of any angular momentum obey such commutation rules. Consequently, we can apply the ideas presented in Section 11.2.3 to $\hat{\boldsymbol{I}}_{1-3}$ and define two ladder operators

$$\hat{I}_{s,1-3}{}^{\pm} = \hat{I}_{\xi,1-3} \pm i\hat{I}_{\eta,1-3} = \hat{I}_{s,1}{}^{\pm} + \hat{I}_{s,2}{}^{\pm} + \hat{I}_{s,3}{}^{\pm} \qquad (13\text{-}243)$$

by analogy with Eq. (11-35). In Eq. (13-243) we have used the fact that

$$\hat{I}_{\gamma,1-3} = \hat{I}_{\gamma,1} + \hat{I}_{\gamma,2} + \hat{I}_{\gamma,3} \qquad (13\text{-}244)$$

for $\gamma = \xi, \eta, \zeta$; $\hat{I}_{\gamma,\alpha}$ is the γ component of the spin of proton α [= 1, 2, or 3], so that

$$\hat{I}_{s,\alpha}{}^{\pm} = \hat{I}_{\xi,\alpha} \pm i\hat{I}_{\eta,\alpha}. \qquad (13\text{-}245)$$

If we apply $\hat{I}_{s,1-3}{}^{-}$ to the function $|1;3/2,3/2\rangle = \Phi_{\mathrm{ns}}^{(1)}$, the resulting function will be proportional to $|1;3/2,1/2\rangle$ by analogy with Eq. (11-38). Since $|1;3/2,3/2\rangle$ has A_1' symmetry in $\boldsymbol{D}_{3\mathrm{h}}(\mathrm{M})$ and $\hat{I}_{s,1-3}{}^{-}$ is invariant to permutations of the three protons and to inversion, it follows that $|1;3/2,1/2\rangle$ also has A_1' symmetry in $\boldsymbol{D}_{3\mathrm{h}}(\mathrm{M})$. By applying $\hat{I}_{s,1-3}{}^{-}$ to $|1;3/2,1/2\rangle$ we can show that $|1;3/2,-1/2\rangle$ has A_1' symmetry, and finally by applying $\hat{I}_{s}{}^{-}$ to $|1;3/2,-1/2\rangle$ we confirm the obvious result [see Eq. (8-4)] that $|1;3/2,-3/2\rangle = \Phi_{\mathrm{ns}}^{(8)}$ has A_1' symmetry. Thus, the four functions $|1;3/2,m_{I,1-3}\rangle$, $m_{I,1-3} = -3/2, -1/2, 1/2, 3/2$, all have A_1' symmetry. We know from Eq. (8-7) that the eight functions in Eq. (8-4) span the reducible representation $4A_1' + 2E'$ in $\boldsymbol{D}_{3\mathrm{h}}(\mathrm{M})$, and since we have just shown that the four A_1' functions all have $I_{1-3} = 3/2$, the two function pairs $|0;1/2,m_{I,1-3}\rangle$ and $|1;1/2,m_{I,1-3}\rangle$, $m_{I,1-3} = -1/2$ or $1/2$, both must have E' symmetry. From these results, the symmetry of the total spin functions $|I_{1-2}, I_{1-3}; I, m_I\rangle$ of $^{14}NH_3$ can be straightforwardly derived, since the ^{14}N spin functions are totally symmetric in the MS group. The symmetry of the function $|I_{1-2}, I_{1-3}; I, m_I\rangle$ is the same as that of the proton spin function $|I_{1-2}; I_{1-3}, m_{I,1-3}\rangle$.

For a molecule with three protons and no other equivalent nuclei, we can determine the MS group symmetries of the basis functions $\Phi_{\mathrm{erns}}^{(e,F,I,N,J,S,k,m_F)}$ in Eq. (13-221) from the known symmetries of the $\Phi_{\mathrm{er}}^{(e,N,S,J,k,m_J)}$ functions and from the symmetries of the nuclear spin functions $\Phi_{\mathrm{nspin}}^{(I,m_I)} \equiv |I_{1-2}, I_{1-3}; I, m_I\rangle$ just derived. Symmetry arguments of the type employed here for $^{14}NH_3$ are often helpful in determining the MS group transformation properties of the $\Phi_{\mathrm{nspin}}^{(I,m_I)}$ functions. However, in general it may be necessary to derive the detailed form of these functions by repeated use of Eq. (10-98) in order to determine their MS group symmetries.

We discuss the most important effects of the hyperfine Hamiltonian $\hat{H}_{\mathrm{hfs}}$. Our treatment is limited to isolated singlet electronic states, for which we can take the total internal Hamiltonian to be $\hat{H}_{\mathrm{rve}} + \hat{H}_{\mathrm{hfs}}$.

The contribution to the total molecular energy from the hyperfine term $\hat{H}_{\mathrm{hfs}}$ is extremely small, and usually it is a satisfactory approximation to obtain first the eigenvalues and eigenfunctions of the Hamiltonian $\hat{H}_{\mathrm{rve}}$ and then to consider the hyperfine effects in one such particular rovibronic state characterized by the quantum number N. That is, we neglect the interaction between the rovibronic state under study and all other rovibronic states.

In the singlet state under study, the electronic wavefunction is $\Phi_{\mathrm{elec}}^{(e,0,0)}$. The eigenfunctions of $\hat{H}_{\mathrm{rve}}$ can be expressed as indicated by Eq. (13-217)

$$\Phi_{\mathrm{rve}}^{(N,m)} = \Phi_{\mathrm{elec}}^{(e,0,0)} \sum_{V,L,k} c_{eVLk}^{(N)} \Phi_{\mathrm{vib}}^{(V,L)} \, |N,k,m\rangle \,, \tag{13-246}$$

where the sum over e is omitted since the electronic state under study is isolated. When we neglect the hyperfine interactions between the rovibronic state $\Phi_{\mathrm{rve}}^{(N,m)}$ and all other rovibronic states, we can express the eigenfunctions of $\hat{H}_{\mathrm{rve}} + \hat{H}_{\mathrm{hfs}}$ in the form

$$\Phi_{\mathrm{int}} = \sum_{\mathcal{I},I} c_{\mathcal{I},I}^{(F)} \Phi_{\mathrm{rvens}}^{(\mathcal{I},I,N,F,m_F)} \tag{13-247}$$

with [see Eq. (10-98)]

$$\Phi_{\mathrm{rvens}}^{(\mathcal{I},I,N,F,m_F)} = \sum_{m=-N}^{N} \sum_{m_I=-I}^{I} (-1)^{N-I+m_F} \sqrt{2F+1} \times \begin{pmatrix} N & I & F \\ m & m_I & -m_F \end{pmatrix} \Phi_{\mathrm{nspin}}^{(\mathcal{I},I,m_I)} \, \Phi_{\mathrm{rve}}^{(N,m)} \,, \tag{13-248}$$

where we have indicated that the nuclear spin function is labeled by the "intermediate" spin quantum numbers $\mathcal{I}$. Since $\hat{\boldsymbol{S}} = 0$, we have here $\hat{\boldsymbol{F}} = \hat{\boldsymbol{N}} + \hat{\boldsymbol{I}}$.

As indicated by Eq. (13-248), we obtain the eigenvalues and eigenfunctions of $\hat{H}_{\mathrm{rve}} + \hat{H}_{\mathrm{hfs}}$ by diagonalizing its matrix representation in the basis set $\Phi_{\mathrm{rvens}}^{(\mathcal{I},I,N,F,m_F)}$. The matrix elements have the form

$$\left\langle \Phi_{\mathrm{rvens}}^{(\mathcal{I},I,N,F,m_F)} \middle| \hat{H}_{\mathrm{rve}} + \hat{H}_{\mathrm{hfs}} \middle| \Phi_{\mathrm{rvens}}^{(\mathcal{I}',I',N,F,m_F)} \right\rangle = E_{\mathrm{rve}} \, \delta_{\mathcal{I}\mathcal{I}'} \, \delta_{II'} + \left\langle \Phi_{\mathrm{rvens}}^{(\mathcal{I},I,N,F,m_F)} \middle| \hat{H}_{\mathrm{hfs}} \middle| \Phi_{\mathrm{rvens}}^{(\mathcal{I}',I',N,F,m_F)} \right\rangle , \tag{13-249}$$

where E_{rve} is the eigenvalue of $\hat{H}_{\mathrm{rve}}$ corresponding to the eigenfunction in Eq. (13-246). The resulting matrix is block diagonal in F and m_F, and the matrix elements are independent of m_F since it quantizes the projection of $\hat{\boldsymbol{F}}$ onto an arbitrarily chosen space fixed axis.

The microscopic form of $\hat{H}_{\mathrm{hfs}}$, involving the spins and angular momenta of the individual nuclei, is indicated in Chapter 7 [see Table 7-1]. In analyses of experimental spectra, the hyperfine effects are usually described using an effective Hamiltonian expressed in terms of the rovibronic angular momentum $\hat{\boldsymbol{N}}$ (called $\boldsymbol{J}$ for singlet states). This Hamiltonian is the sum of three terms:

$$\hat{H}_{\mathrm{hfs}} = \hat{H}_{\mathrm{quad}} + \hat{H}_{\mathrm{nsr}} + \hat{H}_{\mathrm{nss}} . \tag{13-250}$$

In Eq. (13-250), the term $\hat{H}_{\mathrm{quad}}$, that describes the quadrupole coupling, is defined in Eq. (7-24). The term $\hat{H}_{\mathrm{nsr}}$ that describes the interaction between the nuclear spins and the over-all rotation of the molecule is given by

$$\hat{H}_{\text{nsr}} = \sum_{\alpha} c_{\alpha}\, \hat{\boldsymbol{I}}_{\alpha} \cdot \hat{\boldsymbol{N}}. \tag{13-251}$$

The parameters c_{α} in Eq. (13-251) depend on the actual rovibronic state considered. The third term, $\hat{H}_{\text{nss}}$, accounts for the interactions between nuclear spins and is expressed as

$$\hat{H}_{\text{nss}} = \sum_{\alpha<\beta} S_{\alpha\beta} \left\{ \frac{3}{2} \left[\left(\hat{\boldsymbol{I}}_{\alpha} \cdot \hat{\boldsymbol{N}}\right) \left(\hat{\boldsymbol{I}}_{\beta} \cdot \hat{\boldsymbol{N}}\right) + \left(\hat{\boldsymbol{I}}_{\beta} \cdot \hat{\boldsymbol{N}}\right) \left(\hat{\boldsymbol{I}}_{\alpha} \cdot \hat{\boldsymbol{N}}\right) \right] - \left(\hat{\boldsymbol{I}}_{\alpha} \cdot \hat{\boldsymbol{I}}_{\beta}\right) \hat{\boldsymbol{N}}^2 \right\}. \tag{13-252}$$

The parameters $S_{\alpha\beta}$ of $\hat{H}_{\text{nss}}$ depend on the rovibronic state considered.

The matrix elements of $\hat{H}_{\text{quad}}$ between the basis functions in Eq. (13-222) depend on the coupling constants $eQq_{NN}^{(\alpha)}$ for the rovibronic state in question [see, for example, Cook and De Lucia (1971)]. Here, eQ is the quadrupole moment of nucleus α and $q_{NN}^{(\alpha)}$, which determines the expectation values of the electric field gradient components $V_{ab}^{(\alpha)}$ [see Eq. (7-24)] in the rovibronic state under study, is defined in Eq. (18) of Cook and De Lucia (1971).

In order to calculate $q_{NN}^{(\alpha)}$ and the parameters c_{α} and $S_{\alpha\beta}$ in Eqs. (13-251) and (13-252), respectively, we must average the hyperfine Hamiltonian $\hat{H}_{\text{hfs}}$ over the rovibronic wavefunction. In this calculation, it is normally a satisfactory approximation to take the rovibronic wavefunction to be separable [see Eq. (13-1)]. Thus, for calculating the matrix elements on the right hand side of Eq. (13-249), we employ the rovibronic wavefunction $\Phi_{\text{elec}}^{(e,0,0)}\Phi_{\text{rot}}\Phi_{\text{vib}}$, where $\Phi_{\text{rot}}\Phi_{\text{vib}}$ is the rotation-vibration wavefunction obtained when rotation-vibration interaction is neglected. In this approximation, $eQq_{NN}^{(\alpha)}$ can be obtained from Eq. (3) of Thaddeus, Krisher, and Loubser (1964)

$$eQq_{NN}^{(\alpha)} = 2eQ \sum_{\gamma=x,y,z} \frac{\left\langle \Phi_{\text{vib}}\Phi_{\text{elec}}^{(e,0,0)} \middle| V_{\gamma\gamma}^{(\alpha)} \middle| \Phi_{\text{vib}}\Phi_{\text{elec}}^{(e,0,0)} \right\rangle \left\langle \Phi_{\text{rot}} \middle| \hat{N}_{\gamma}^2 \middle| \Phi_{\text{rot}} \right\rangle}{(N+1)(2N+3)}. \tag{13-253}$$

In analyses of experimental spectra, it is customary to use the notation

$$\chi_{\gamma\gamma}^{(\alpha)} = \left\langle \Phi_{\text{vib}}\Phi_{\text{elec}}^{(e,0,0)} \middle| V_{\gamma\gamma}^{(\alpha)} \middle| \Phi_{\text{vib}}\Phi_{\text{elec}}^{(e,0,0)} \right\rangle. \tag{13-254}$$

The values of the ***quadrupole coupling constants*** $\chi_{\gamma\gamma}^{(\alpha)}$ ($\gamma = x, y, z$) are determined by fitting to experiment. An "exact" calculation of the $q_{NN}^{(\alpha)}$ parameters for the molecules H_2D^+, HD_2^+, and D_3^+ from first principles, starting from Eq. (18) of Cook and De Lucia (1971) and using a non-separable rovibronic wavefunction, has been carried out by Jensen, Paidarová, Vojtík, and Špirko (1991).

In the approximation of a separable rovibronic wavefunction, the parameter c_α in Eq. (13-251) is obtained from Eq. (17) of Thaddeus, Krisher, and Loubser (1964)

$$c_\alpha = \sum_{\gamma=x,y,z} \frac{\left\langle \Phi_{\text{vib}}\Phi_{\text{elec}}^{(e,0,0)} \left| M_{\gamma\gamma}^{(\alpha)} \right| \Phi_{\text{vib}}\Phi_{\text{elec}}^{(e,0,0)} \right\rangle \left\langle \Phi_{\text{rot}} \left| \hat{N}_\gamma^2 \right| \Phi_{\text{rot}} \right\rangle}{N(N+1)}, \tag{13-255}$$

The quantities $\left\langle \Phi_{\text{vib}}\Phi_{\text{elec}}^{(e,0,0)} \left| M_{\gamma\gamma}^{(\alpha)} \right| \Phi_{\text{vib}}\Phi_{\text{elec}}^{(e,0,0)} \right\rangle$ are normally determined by fitting to experimental data. The tensor elements $M_{\gamma\gamma}^{(\alpha)}$ are given by Ramsey (1956) [see also Eq. (1) of Jensen, Paidarová, Špirko, and Sauer (1997)]. Finally, the parameter $S_{\alpha\beta}$ in Eq. (13-252) is obtained from Eqs. (9) and (10) of Thaddeus, Krisher, and Loubser (1964)

$$S_{\alpha\beta} = 2 \sum_{\gamma=x,y,z} \frac{\langle \Phi_{\text{vib}} | R_{\gamma\gamma}(\alpha\beta) | \Phi_{\text{vib}} \rangle \left\langle \Phi_{\text{rot}} \left| \hat{N}_\gamma^2 \right| \Phi_{\text{rot}} \right\rangle}{(N+1)(2N+3)N(2N-1)}, \tag{13-256}$$

where the tensor elements $R_{\gamma\gamma}(\alpha\beta)$ are defined as

$$R_{\gamma\gamma}(\alpha\beta) = g_\alpha g_\beta \, \frac{\mu_0 \mu_N^2}{4\pi} \, \frac{r_{\alpha\beta}^2 - 3\left[\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta\right]_\gamma^2}{r_{\alpha\beta}^5}. \tag{13-257}$$

Their matrix elements $\langle \Phi_{\text{vib}} | R_{\gamma\gamma}(\alpha\beta) | \Phi_{\text{vib}} \rangle$ are determined by fitting to experimental data. In Eq. (13-257), $\boldsymbol{r}_\alpha$ and $\boldsymbol{r}_\beta$ are the position vectors of nuclei α and β, respectively, in the molecule fixed axis system xyz. The quantities $[\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta]_\gamma$ are the γ coordinates ($\gamma = x$, y, z) of the vector $\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta$, and $r_{\alpha\beta}$ is the length of this vector, i.e., the instantaneous value of the distance between the nuclei α and β. The nuclear g factor of nucleus α is denoted g_α [see Chapter 7]. The tensor elements $R_{\gamma\gamma}(\alpha\beta)$ do not depend on the electronic coordinates so that in the evaluation of $S_{\alpha\beta}$ from Eq. (13-256) the integration over these coordinates produces the unit normalization integral of the function $\Phi_{\text{elec}}^{(e,0,0)}$.

In order that the matrix elements of $\hat{H}_{\text{quad}}$ or $\hat{H}_{\text{nss}}$ be nonvanishing, it follows from angular momentum theory that the selection rules

$$|\Delta I| \le 2, \;\; |\Delta N| \le 2, \text{ and } |\Delta k| \le 2 \tag{13-258}$$

must be fulfilled, whereas the nonvanishing matrix elements of $\hat{H}_{\text{nsr}}$ satisfy

$$|\Delta I| \le 1, \;\; |\Delta N| \le 1, \text{ and } |\Delta k| \le 1. \tag{13-259}$$

The matrix elements are most conveniently calculated by expressing the operators $\hat{H}_{\text{quad}}$, $\hat{H}_{\text{nss}}$, and $\hat{H}_{\text{nsr}}$ in terms of the irreducible spherical tensor operators briefly discussed in Section 10.3. The matrix elements of a Hamiltonian expressed in this form can be derived using angular momentum theory [essentially by using the Wigner-Eckart theorem] without considering the detailed form of the basis functions [see, for example, Thaddeus, Krisher, and Loubser (1964) and Cook and De Lucia (1971)].

The effect of $\hat{H}_{\rm hfs}$ will be to make a rovibronic energy level [i.e., an eigenstate of $\hat{H}_{\rm rve}$] split into a number of ***hyperfine energies***, each one characterized by a value of F. The energy splittings between these components will be extremely small compared to a typical difference between two rovibronic energies.[17] The parity of the internal wavefunctions $\Phi_{\rm int}$ in Eq. (13-247) is determined entirely by the rovibronic eigenfunction $\Phi_{\rm rve}^{(N,m)}$ in Eq. (13-246) since nuclear spin wavefunctions are unaffected by inversion. Consequently, all the wavefunctions $\Phi_{\rm int}$ belonging to the hyperfine components of a given rovibronic state will have the same symmetry in the MS group. This symmetry will be $\Gamma_{\rm MS}^{+}$ or $\Gamma_{\rm MS}^{-}$; these two symmetries are allowed by the Pauli exclusion principle [see Chapter 8].

13.6.3 Ortho-para conversion

In an H_2 molecule the spins of the two protons can couple to produce states with $I = 0$ (para-H_2) and $I = 1$ (ortho-H_2).[18] In the electronic ground state of H_2 it follows from the Pauli exclusion principle that levels with N $(=J)$ even have + parity and are para levels, and levels with N $(=J)$ odd have − parity and are ortho levels. Since ortho and para levels have opposite parity for H_2 the ortho/para nature is a conserved quantity for isolated H_2 molecules in field free space.[19] However, intermolecular interactions, and collisions with the walls of a containing vessel, put the molecule in an inhomogeneous magnetic field so that noticeable ortho-para conversion can occur. Because of this if hydrogen gas is maintained at a cold temperature long enough it will eventually reach thermal equilibrium and convert to almost pure $N = 0$ (i.e. para) hydrogen. In practice to obtain para hydrogen a paramagnetic 'catalyst' such as O_2 or active charcoal is added to hasten the process of flipping the nuclear spin [see, for example, Farkas and Sandler (1940)].

In most polyatomic molecules it is possible that ***within a given vibrational state*** internal states $\Phi_{\rm int}$ having different nuclear spin symmetries, can have the same symmetry in the MS group. When this is the case ortho and para levels can come into resonance and be coupled significantly by $\hat{H}_{\rm hfs}$. This coupling connects different rotational states, and we neglect this possibility in the discussion of hyperfine structure above. In the calculation of hyperfine structure this is usually a satisfactory approximation, but it will not be satisfactory in the circumstance we discuss here (see also Section 17.7 in which ortho and para states of different electronic states come close in energy). Thermalization of ortho and para states will now occur much more rapidly than in pure hydrogen gas. Even so ortho-para mixing, and ortho-para transitions, are studied in this situation, and methods for the separation of spin isomers have been developed; one example is a method based on light-induced drift (LID) [for a review see Hermans (1992)].

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[17] However, see Bordé and Bordé (1982) for an exceptional case involving the SF_6 molecule. For a spherical top molecule such as SF_6 nuclear hyperfine splittings can be of the same order of magnitude as centrifugal distortion splittings; such small centrifugal distortion splittings are called superfine splittings.

[18] It is conventional to call the spin state having the higher spin statistical weight the ortho state.

[19] But if we consider excited electronic states then extremely weak ortho-para interactions can occur in H_2; see the Bibliographical Notes to Chapter 14.

We use CH_3F as an example. In CH_3F [MS group $\boldsymbol{C}_{3v}(M)$; see Table A-6] the spins of the three protons (labeled 1, 2, and 3) couple according to Eqs. (13-234) and (13-235). The quantum number I_{1-3} associated with $\hat{\boldsymbol{I}}_{1-3}{}^2$ can have the value 3/2 (ortho-CH_3F) and 1/2 (para-CH_3F). We can use exactly the same arguments to prove that nuclear spin functions with $I_{1-3} = 3/2$ have A_1 symmetry in $\boldsymbol{C}_{3v}(M)$, and nuclear spin functions with $I_{1-3} = 1/2$ have E symmetry in $\boldsymbol{C}_{3v}(M)$, as used above for $^{14}NH_3$ in $\boldsymbol{D}_{3h}(M)$. The one spin function of ^{12}C ($I_C = 0$) and the two spin functions of ^{19}F ($I_F = 1/2$) are all totally symmetric in $\boldsymbol{C}_{3v}(M)$. The total representation generated by all 16 possible nuclear spin functions is

$$\Gamma_{\text{nspin}}^{\text{tot}} = 8A_1 \oplus 4E. \tag{13-260}$$

Table 13-4

The statistical weights of the rovibronic states of $^{12}CH_3F$

Γ_{rve}	Γ_{nspin}	Γ_{int}	Statistical weight
A_1	$8A_1$;–	A_1; A_2	8
A_2	–;$8A_1$	A_1; A_2	8
E	$4E$;$4E$	A_1; A_2	8

The vibronic ground state of CH_3F has A_1 symmetry, and thus the symmetry of the rovibronic states comes directly from Table 12-5. Application of the Pauli exclusion principle leads to the result that for a given value of F there can be both ortho and para states belonging to each of the two allowed symmetries A_1 and A_2 in $\boldsymbol{C}_{3v}(M)$. The allowed rovibronic-state/nuclear-spin-state combinations, and the nuclear spin statistical weights, are given in Table 13-4 for CH_3F. Using these results we see that, for example, a $K = 3$ state ($\Gamma_{\text{rve}} = A_1 \oplus A_2$) has to be in an ortho spin state ($\Gamma_{\text{ns}} = 8A_1$) to give internal states having symmetry A_1 and A_2, and a $K = 1$ state ($\Gamma_{\text{rve}} = E$) has to be in a para spin state ($\Gamma_{\text{ns}} = 4E$) which also leads to internal states of symmetry A_1 and A_2. Since the internal state symmetries are the same these ortho and para states can be coupled by the $\hat{H}_{\mathrm{hfs}}$ terms in the molecular Hamiltonian. These spin isomers can be separated in LID experiments, and the rate of equilibration can be monitored using absorption spectroscopy [see Nagels, Calas, Roozemond, Hermans, and Chapovsky (1996) and references therein]. For $^{13}CH_3F$ (see below) the ortho/para labeling of the rotational states is the same as for $^{12}CH_3F$, but the number of states is doubled because ^{13}C has $I = 1/2$. Equations (13-258) and (13-259) show that the hyperfine Hamiltonian $\hat{H}_{\mathrm{hfs}}$ can couple ortho and para states with different N values. The coupling matrix elements can be derived as outlined by Curl, Kasper, and Pitzer (1967).

The mechanism for ortho-para conversion in a molecule such as CH_3F, whose ortho and para levels are coupled by $\hat{H}_{\mathrm{hfs}}$, was first proposed by Curl, Kasper, and Pitzer (1967) [see also Chapovsky (1996)] and can be summarized as follows. A molecule can collide with its environment and these collisions can cause transitions between molecular states. It is unlikely that a collision will flip the spin and interconvert ortho and para states directly. However, a collision can rather easily take the molecule from a pure ortho state, say, to another ortho state that is significantly coupled with a para state by $\hat{H}_{\mathrm{hfs}}$. In such a coupled state time-dependent quantum mechanics describes the molecule as oscillating between the ortho and para components of its wavefunction. Thus, when the molecule has a high probability of being in the para component another collision can carry it off to a pure para state. Chapovsky (1996) has termed this process ***quantum relaxation***.

The net effect of quantum relaxation is to transfer the molecule from a pure ortho state to a pure para state, or vice versa. The ortho-para state pairs coupled by $\hat{H}_{\mathrm{hfs}}$ serve as "gateways" for the conversion. and the conversion rate is critically dependent on the energy differences between the coupled ortho and para states. In order that the small matrix elements of $\hat{H}_{\mathrm{hfs}}$ can produce a significant mixing, the interacting states must be very close in energy. The CH_3F molecule (and in particular the $^{13}CH_3F$ isotopomer) has proved a favorable case for ortho-para conversion because it has suitable gateway states. According to the most accurate rotation-vibration parameters currently available for $^{13}CH_3F$ [Papoušek, Demaison, Wlodarczak, Pracna, Klee, and Winnewisser (1994)] the $(N = J, K) = (11,1)$ and $(9,3)$ levels are separated by 130.014 MHz, and the $(21,1)$ and $(20,3)$ levels are separated by 352.003 MHz. Each nucleus in $^{13}CH_3F$ has zero quadrupole moment so $\hat{H}_{\mathrm{quad}}$ vanishes. Ortho-para mixing, and ortho-para transitions, are discussed for the ammonia molecule in Section 15.4.1, for H_2^+ in Section 17.7, and for H_2^+ and methane in Section 14.1.16.

13.6.4 Combined effects of electron and nuclear spin

As indicated in Chapter 7 the hyperfine Hamiltonian $\hat{H}_{\mathrm{hfs}}$ contains the term $\hat{H}_{\mathrm{nses}}$ that describes the interaction between the electron spins and the nuclear spins. This term can be important in electronic states with $S > 0$. Bowater, Brown, and Carrington (1973) give the matrix elements associated with the most important interactions of this type in their Eq. (31). In Chapter 17 we briefly consider the Fermi contact interaction operator [see Eq. (17-130)] which causes g and u electronic states to interact in H_2^+.

BIBLIOGRAPHICAL NOTES

Reduced Hamiltonians

Watson (1967, 1977). The problem of indeterminacy of the centrifugal distortion constants for an asymmetric top molecule is solved by a reduction of the effective rotational Hamiltonian.

Perevalov and Tyuterev (1982). Reduced Hamiltonians are derived for asymmetric top molecules in the presence of accidental resonances.

Lobodenko, Sulakshina, Perevalov, and Tyuterev (1987). Reduced Hamiltonians for symmetric top molecules of C_{3v} symmetry.

Tyuterev, Champion, and Pierre (1990). This paper (see also the references cited in it) treats reduced Hamiltonians for spherical top molecules.

Teffo, Sulakshina, and Perevalov (1992). Reduced Hamiltonians for the linear molecule CO_2.

Sarka, Papoušek, Demaison, Mäder, and Harder (1997). An excellent review article treating a variety of subjects. It gives a very good explanation of the reduction technique and presents reduced Hamiltonians for symmetric top molecules.

The variational approach

Rotation-vibration calculations based on geometrically defined vibrational coordinates are described in the following review articles:

Carney, Sprandel, and Kern (1978).
Carter and Handy (1986).
Tennyson (1986).
Bačić and Light (1989).
Jensen (1992).

A selection of examples of rotation-vibration calculations carried out with kinetic energy operators expressed in terms of geometrically defined vibrational coordinates is given here:

Bačić and Light (1986). The DVR-DGB method developed and applied to LiCN/LiNC (with the CN distance fixed).

Bačić and Light (1987). The DVR-DGB method applied to HNC/HCN with all vibrational modes included.

Tennyson and Henderson (1989), Henderson, Tennyson and Sutcliffe (1993). DVR approach applied to H_3^+.

Mladenović and Bačić (1990). The DVR-DGB approach applied to HCN/HNC.

Bentley, Wyatt, Menou, and Leforestier (1992). Vibrational energies of planar HCCH calculated with a DVR approach.

Bačić and Zhang (1992). Variational calculation of the rovibrational energies of H_3^+.

Bramley and Handy (1993). Rovibrational energies of HCCH, HOOH, and HCNO are calculated in a variational approach with a kinetic energy operator expressed in terms of geometrically defined vibrational coordinates.

Tennyson (1993). The DVR approach applied to H_2S, H_2O, and H_3^+.

Carter, Mills, and Handy (1993). Variational calculations of rovibrational energies in the electronic ground state of HCN. The potential energy function is refined in least-squares fittings of experimental data.

McNichols and Carrington (1993). Vibrational energies for H_2CO calculated variationally by means of a method for diagonalizing sparse matrices.

Tennyson (1995). A review article on the H_3^+ molecular ion. Owing to the low mass of the protons, the vibrational amplitudes in H_3^+ are not small compared to the linear dimensions of the equilateral triangular equilibrium configuration. Thus the standard theory breaks down for this molecule, but rotation-vibration calculations based on geometrically defined vibrational coordinates have been extremely successful.

Polyansky, Jensen, and Tennyson (1996). Refinement of the potential energy surface of the electronic ground state of H_2O in least-squares fittings to experimental data.

Partridge and Schwenke (1997). Highly accurate *ab initio* calculation of the potential energy surface for the electronic ground state of H_2O, combined with a variational calculation of the rotation-vibration energies. The potential energy surface is optimized slightly in a least-squares fitting to experimental data.

Carter, Handy, and Demaison (1997). Rovibrational energies of H_2CO are calculated in a variational approach with a kinetic energy operator expressed in terms of geometrically defined vibrational coordinates, and the potential energy function is refined in least-squares fittings of experimentally derived energies.

Polyansky, Zobov, Viti, Tennyson, Bernath, and Wallace (1997). Application of variational calculations to the simulation of high-temperature spectra of water and comparison with experiment; this theoretical work has greatly improved the understanding of the experimental spectra coming from the laboratory and from the Sun.

The Renner effect

There is a vast literature on the Renner effect, and the following papers represent a selection.

Renner (1934). Renner uses perturbation theory to develop an effective Hamiltonian involving the 'Renner parameter' ϵ, which satisfies $|\epsilon|<1$. He uses numerical methods to calculate energies $E(\epsilon, v, K)$ for intermediate and large values of ϵ assuming harmonic oscillator bending potentials as depicted in Fig 13-6a.

Pople and Longuet-Higgins (1958). A new form of the effective Hamiltonian is formulated from symmetry considerations of a simplified one-electron model, and this Hamiltonian is used to interpret the electronic spectrum of NH_2 obtained by Dressler and Ramsay (1959).

Pople (1960). The theory of Pople and Longuet-Higgins (1958) is extended to take into account spin–orbit coupling.

Hougen (1962a). Expressions for the rovibronic energies of linear triatomic molecules in $^2\Pi$ electronic states are derived.

Hougen (1962b). The theory of Hougen (1962a) is extended to the case of a Fermi resonance.

Hougen and Jesson (1963). A short note discussing anharmonic corrections for linear triatomic molecules exhibiting the Renner effect.

Barrow, Dixon, and Duxbury (1974). The paper discusses a model Hamiltonian which combines the effects of large amplitude bending vibration in a bent triatomic molecule with those arising from the Renner effect and from spin–orbit coupling.

Jungen and Merer (1976, 1980). The Renner effect treated in the formalism of Hougen, Bunker, and Johns (1970) [see Chapter 15].

Brown (1977). An effective vibronic Hamiltonian is derived for a linear triatomic molecule in a Π electronic state.

Duxbury and Dixon (1981). It is shown by numerical examples that the methods for treating the Renner effect developed by Barrow, Dixon, and Duxbury (1974) and by Jungen and Merer (1980) are equivalent.

Perić, Peyerimhoff, and Buenker (1983). A treatment of the Renner effect by diagonalization of the matrix representation of an effective Hamiltonian.

Brown and Jørgensen (1983). This paper reverts to Renner's original 1934 treatment and formulates it in such a manner that the construction of the effective Hamiltonian from the real one becomes clear. They show that it is simple to construct the effective Hamiltonian in a consistent and logical fashion, and indicate how further corrections can be included when required by experiments with higher resolution. In this way Renner's original formulation can be applied to any of the situations depicted in Fig. 13-6. The perturbation theory approach is developed to fourth order and spin-orbit coupling is included.

Carter and Handy (1984). A theoretical procedure based on the rotation-vibration Hamiltonian in Eqs. (13-138) and (13-139), which is expressed in terms of geometrically defined vibrational coordinates. The Hamiltonian is extended to account for the effects of the electronic angular momentum, and the eigenvalues of the extended Hamiltonian are obtained in a variational calculation.

Duxbury and Jungen (1988). An analysis of experimental data for the $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ electronic states of CH_2, using the approach of Jungen and Merer (1980).

Jensen, Brumm, Kraemer, and Bunker (1995a). A procedure is developed for the calculation of rovibronic energy levels subject to the Renner effect and spin-orbit coupling in a triatomic molecule. The kinetic energy is set up as in the MORBID (Morse Oscillator Rigid Bender Internal Dynamics) Hamiltonian (see Section 15.4.7) but with $\hat{N}_z$ replaced by $\hat{N}_z - \hat{L}_z$. The Hamiltonian is diagonalized in a basis that consists of products of three types of wavefunction: (a) Vibrational stretching eigenfunctions obtained by diagonalizing the stretching part of the full Hamiltonian in a Morse oscillator basis [see Eq. (35)], (b) Numerical rigid-bender bending wavefunctions that come from the numerical diagonalization of the bending Hamiltonian at each K value [see Eq. (34)], and (c) Electron orbital-electron spin-rotation functions that are linear combinations of Born-Oppenheimer products of electronic orbital, and Hund's case (b) electron spin and rotation wavefunctions [see Eqs. (28) and (29)]. The functions (c) are obtained in a preliminary diagonalization of the electronic motion and the z axis rotation part of the full Hamiltonian [see Eq. (27)]; the idea of forming the basis functions (c) was suggested by Barrow, Dixon, and Duxbury (1974). The procedure is tested by applying it to the calculation of the energy levels of the $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ states of CH_2 using *ab initio* data from Green, Handy, Knowles and Carter (1991).

Kolbuszewski, Bunker, Kraemer, Osmann, and Jensen (1996). This is a modification of the work of Jensen, Brumm, Kraemer, and Bunker (1995a) (called JBKB) that is particularly necessary for linear/quasilinear systems such as BH_2 and CH_2^+. In this modification the Hamiltonian is diagonalized in expansion functions [see Eq. (11)] that are linear combinations of the product functions used in JBKB as a basis. The coefficients in these expansion functions are the eigenvectors obtained by diagonalizing the Hamiltonian without the spin–orbit coupling term in a limited set (in which $K = N$) of the product functions. The technique is used to calculate the energy levels of the $\tilde{X}\,^2A_1$ and $\tilde{A}\,^2B_1$ states of BH_2, and they satisfactorily reproduce the experimental results of Herzberg and Johns (1967);it is also used to predict the appearance of the absorption spectrum of CH_2^+ in Osmann, Bunker, Jensen, and Kraemer (1997).

The Jahn-Teller effect

Jahn and Teller (1937).

Longuet-Higgins, Öpik, Pryce, and Sack (1958).

Miller and Bondybey (1983). This paper treats the vibronic effects in detail.

The rotational energy structure in Jahn-Teller electronic states of symmetric tops has been discussed by:

Child and Longuet-Higgins (1961).

Child (1962, 1963).

Brown (1971).

Hougen (1980a). This paper also discusses the vibronic double groups that one would use in classifying double valued vibrational wavefunctions in electronic states subject to the Jahn-Teller effect. The groups are similar to EMS groups (see Chapters 15 and 17). No use of such double groups has yet been made in the literature.

Watson (1984). This paper also treats the rotational energy level structure in Jahn-Teller electronic states of spherical top molecules.

Liu and Miller (1992).

The methoxy radical CH_3O, which exhibits the Jahn-Teller effect in its $\tilde{X}\,^2E$ electronic ground state, has been the subject of very many experimental studies. We give a few recent references to this work:

Foster, Misra, Lin, Damo, Carter, and Miller (1988).
Liu, Damo, Lin, Foster, Misra, Yu, and Miller (1989).
Geers, Kappert, Temps, and Sears (1993).
Geers, Kappert, Temps, and Wiebrecht (1994).
Powers, Pushkarsky, and Miller (1997a,1997b).

The sodium trimer Na_3 exhibits the Jahn-Teller effect in the ground electronic state and in several excited electronic states. The $\tilde{B}$ state is the result of the vibronic coupling of a $^2E'$ and a $^2A_1'$ electronic state; these two states are very close in energy at the $\boldsymbol{D}_{3h}$ geometry. This is essentially a triply degenerate electronic state, but since the degeneracy is not forced by true, i.e., MS group, symmetry (it results from the symmetry of an approximate electronic Hamiltonian) the interaction between the $^2E'$ and $^2A_1'$ states is termed a *pseudo* Jahn-Teller effect; the energy levels in the $\tilde{B}$ state (the lowest of these three states) involve simultaneous rotation and pseudorotation. Some very recent papers on this molecule are listed below. These papers, and the papers to which they refer, give the reader a good introduction to the complexities that can occur when hyperfine structure, fine structure, large amplitude pseudorotation, the Jahn-Teller and the pseudo Jahn-Teller effect have to be taken into account in the analysis of a very high resolution spectrum.

Ernst and Rakowsky (1995).
Higgins, Ernst, Callegari, Reho, Lehmann, and Scoles (1996).
Mayer, Cederbaum, and Köppel (1996).
Ohashi, Tsuura, Hougen, Ernst, and Rakowsky (1997).
Vituccio, Golonzka and Ernst (1997).

Ortho-para conversion

Curl, Kasper, and Pitzer (1967). This pioneering paper suggests that equilibration of different spin isomers takes place through molecular states mixed by spin-rotation and spin-spin interaction.

Chapovsky (1991, 1996). A mechanism similar to that proposed by Curl, Kasper, and Pitzer (1967) is used to predict the ortho-para conversion rates in CH_3F.

Nagels, Calas, Roozemond, Hermans, and Chapovsky (1996). It is shown that by subjecting $^{13}CH_3F$ molecules to an external electric field [a *Stark field*, see Chapter 14], which has the effect of changing the energy differences between the interacting ortho and para states, large changes in the ortho-para conversion rates can be induced.

Nagels, Bakker, Hermans, and Chapovsky (1998). Experimental data on the temperature dependence of the ortho-para conversion rate of both $^{12}CH_3F$ and $^{13}CH_3F$ are presented for temperatures in the range 300–900 K. The results are qualitatively modeled assuming the mixing to be due to nuclear spin-spin coupling.

14

Transition Intensities and Optical Selection Rules

*The rigorous, or strict, selection rules for one-photon electric dipole transitions for an isolated molecule are derived using the symmetry labels from the MS and **K**(spatial) groups. The more restrictive selection rules obtained by making approximations are discussed, and this leads to the definition of a forbidden transition. At the end of the chapter, magnetic dipole transitions, electric quadrupole transitions, multiphoton processes (including the Raman effect), the Zeeman effect, and the Stark effect are briefly considered. Throughout we use N as the rovibronic angular momentum quantum number consistently, even for singlet states, as in Sections 10.3 and 13.6.*

14.1 ELECTRIC DIPOLE TRANSITIONS

For an isolated molecule an electric dipole transition with the absorption or emission of radiation can only occur between certain pairs of energy levels. The restrictions defining the pairs of energy levels between which such transitions can occur are called selection rules. We can determine rigorous, or strict, selection rules on the true symmetry labels (Γ_{int} and F) by using the MS and **K**(spatial) groups. If we make appropriate approximations we can determine much more restrictive selection rules on near quantum numbers and near symmetry labels. Transitions that are not allowed by these restrictive selection rules, but that are allowed if no approximations are made (or when magnetic dipole and electric quadrupole radiation are considered), are called forbidden transitions.[1] Forbidden transitions are usually weak and the main features of the electromagnetic spectrum of a molecule can be understood without considering them. We derive both the rigorous (strict) selection rules and the more restrictive selection rules obtained after making approximations. The effect of the breakdown of the approximations in allowing forbidden transitions to occur is explained.

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[1] Forbidden transitions have to be distinguished from transitions that are not allowed by the rigorous selection rules on Γ_{int} and F; the latter are said to be *strictly* forbidden as electric dipole transitions.

14.1.1 The line strength

If a parallel monochromatic beam of electromagnetic radiation of initial intensity $I_0(\tilde{\nu})$ at the wavenumber $\tilde{\nu}$ traverses a length ℓ of a gas of absorbing molecules with concentration[2] c^*, the remaining (i.e., transmitted) intensity $I_{\rm tr}(\tilde{\nu})$ is given by the *Lambert-Beer law*

$$I_{\rm tr}(\tilde{\nu}) = I_0(\tilde{\nu})\,\exp\left[-\ell c^* \epsilon(\tilde{\nu})\right], \tag{14-1}$$

where $\epsilon(\tilde{\nu})$ is the (napierian) absorption coefficient. The transmittance τ is defined as

$$\tau = \frac{I_{\rm tr}(\tilde{\nu})}{I_0(\tilde{\nu})} = \exp\left[-\ell c^* \epsilon(\tilde{\nu})\right], \tag{14-2}$$

and we have plotted it, for example, against wavenumber for several NCCN isotopomers in Fig. 8-1 on page 163. If we assume the absorbing molecules to be in thermal equilibrium at the absolute temperature T, the integrated absorption coefficient for an electric dipole transition from an initial state with energy E'' to a final state with energy E' is given by [Smith, Rinsland, Fridovich, and Rao (1985)]

$$\begin{aligned} I(f \leftarrow i) &= \int_{\rm Line} \epsilon(\tilde{\nu})d\tilde{\nu} \\ &= \frac{8\pi^3 N_A \tilde{\nu}_{if} \exp(-E''/kT)[1-\exp(-hc\tilde{\nu}_{if}/kT)]}{(4\pi\epsilon_0)\,3hcQ} S(f \leftarrow i), \end{aligned} \tag{14-3}$$

which depends on the Avogadro constant N_A, the Boltzmann constant k, the Planck constant h, the speed of light in vacuum c, the permittivity of vacuum ϵ_0, the wavenumber of the transition (in cm^{-1}) $\tilde{\nu}_{if} = (E' - E'')/hc$, and the partition function Q given by

$$Q = \sum_w g_w \exp(-E_w/kT). \tag{14-4}$$

In Eq. (14-4), E_w is the energy and g_w the total degeneracy of the state w and the summation extends over all such states of the molecule. The line strength $S(f \leftarrow i)$ of an electric dipole transition is defined as

$$S(f \leftarrow i) = \sum_{\Phi'_{\rm int},\Phi''_{\rm int}} \sum_{A=X,Y,Z} |\langle \Phi'_{\rm int}|\mu_A|\Phi''_{\rm int}\rangle|^2 \tag{14-5}$$

where $\Phi'_{\rm int}$ and $\Phi''_{\rm int}$ are eigenfunctions of the molecular Hamiltonian corresponding to the eigenvalues E' and E'', respectively. In the case of degeneracies, that is if there is more than one eigenfunction $\Phi'_{\rm int}$ (or $\Phi''_{\rm int}$) corresponding to the eigenvalue E' (or E''), we obtain the line strength by adding the individual transition probabilities for all transitions between the degenerate states; this is indicated by the sum over $\Phi'_{\rm int}$ and $\Phi''_{\rm int}$ in Eq. (14-5). In this equation, μ_A is the component of the molecular dipole moment operator along the A axis ($A = X, Y$, or Z); the (X, Y, Z) axis system having origin at the molecular center of mass and space fixed orientation (see Section 10.1.2). This operator is given by

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[2] Named c^* to distinguish it from the speed of light in vacuum c.

$$\mu_A = \sum_j e_j A_j \qquad (14\text{-}6)$$

with e_j and A_j as the charge and A coordinate of the jth particle in the molecule, where j runs over all nuclei and electrons.

For a neutral molecule the value of $\langle \Phi'_{\rm int}|\mu_A|\Phi''_{\rm int}\rangle$ is independent of the origin of the axis system used for μ and, therefore, one is free to choose this origin at one's convenience. It is appropriate to use the nuclear center of mass as origin (rather than the molecular center of mass) in order that we use the (ξ, η, ζ) axis system rather than the (X, Y, Z) axis system (see Section 10.1.2). This is done because the (ξ, η, ζ) axis system is appropriate for setting up the rovibronic wave equation in the Born-Oppenheimer approximation (see Section 10.1). Thus we write the line strength for a neutral molecule as

$$S(f \leftarrow i) = \sum_{\Phi'_{\rm int}, \Phi''_{\rm int}} \sum_{A=\xi,\eta,\zeta} |\langle \Phi'_{\rm int}|\mu_A|\Phi''_{\rm int}\rangle|^2 . \qquad (14\text{-}7)$$

For a molecular ion the dipole moment matrix element $\langle \Phi'_{\rm int}|\mu_A|\Phi''_{\rm int}\rangle$ is not independent of the choice of origin for μ, and the origin should be at the molecular center of mass since this is the origin that results after separating molecular translation. However, since the separation of the nuclear and molecular centers of mass is very small the difference between the line strengths calculated using Eqs. (14-5) and (14-7) for a molecular ion is negligible. However, one has to be careful when one calculates *ab initio* the line strength for a molecular ion, particularly for an otherwise symmetrical ion when it is unsymmetrically isotopically substituted. The effect of this center of mass shift is given in Eqs. (38) and (39) of Jensen (1988c). Two classic examples where this is very important are HD^+ and H_2D^+. For HD^+ the nuclear center of mass is not at the molecular mid-point (as it is for H_2^+) and it has a permanent electric dipole moment [see Eq. (14-85)] of[3] 0.87 D [see Bunker (1974)]. Similarly for H_2D^+ the nuclear center of mass is displaced away from the C_3 axis; H_2D^+ has a permanent electric dipole moment of 0.6 D in its equilibrium configuration and a strong rotational spectrum [see Bogey, Demuynck, Denis, Destombes, and Lemoine (1984)]. Without this effect the dipole moment in HD^+ could arise only from the breakdown of the Born-Oppenheimer approximation, and it would be of the order 10^{-3} times smaller [Bunker (1974)]. Similarly the dipole moment of H_2D^+ could arise only from centrifugal distortion [see, for example, Jensen and

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[3] Where D = debye ≈ 3.33×10^{-30} Cm.

Špirko (1986)] and zero point vibrational effects. Unsymmetrical isotopomers of nonpolar molecular ions such as $HCCD^+$, $CH_2D_2^+$, $H_2CCD_2^+$, and $H_3CCD_3^+$ have dipole moments of 0.30, 0.34, 0.39, and 0.61 D, respectively, which are much larger than the dipole moments of the corresponding neutral isotopomer species ($\approx 10^{-2}$ D) because of this effect.

14.1.2 Rigorous selection rules

For the integrals in Eq. (14-5) not to vanish by symmetry the product of the symmetries of $\Phi_{\rm int}^{\prime *}$ and $\Phi_{\rm int}''$ must contain the symmetry of μ_A from the vanishing integral rule [Eq. (6-140)]. We will use the MS group and the $\boldsymbol{K}$(spatial) group to determine symmetry selection rules. From the definition of μ_A in Eq. (14-6) we see that μ_A is invariant to the permutation of identical nuclei (since identical nuclei have the same charge) and that it is changed in sign by the inversion operation E^* (since $E^* A_j = -A_j$). Thus each of the three dipole moment components μ_ξ, μ_η and μ_ζ transforms as that one-dimensional representation of the MS group that has character +1 under all permutations and character −1 under all permutation inversions; we call this the *electric dipole* representation Γ^* of the MS group. The three translational coordinates T_ξ, T_η and T_ζ also belong to this representation. We can classify μ_ξ, μ_η and μ_ζ in the $\boldsymbol{K}$(spatial) group and they transform as $D^{(1)}$. Thus, for the transition to be an allowed electric dipole transition we must have

$$\Gamma_{\rm int}'' \otimes \Gamma_{\rm int}' \supset \Gamma^* \quad \text{in the MS group,} \tag{14-8}$$

where $\Gamma_{\rm int}''$ and $\Gamma_{\rm int}'$ are the symmetries of $\Phi_{\rm int}''$ and $\Phi_{\rm int}^{\prime *}$, and

$$D_{\rm int}'' \otimes D_{\rm int}' \supset D^{(1)} \quad \text{in the } \boldsymbol{K}\text{(spatial) group,} \tag{14-9}$$

where $D_{\rm int}''$ and $D_{\rm int}'$ are the symmetries of $\Phi_{\rm int}''$ and $\Phi_{\rm int}^{\prime *}$. If the inversion operation E^* is contained in the MS group, or if we are using the CNPI group for classifying the molecular states, the selection rule of Eq. (14-8) can be expressed as a condition on the parities of the wavefunctions $\Phi_{\rm int}$:

$$+ \leftrightarrow -, \qquad + \not\leftrightarrow +, \qquad - \not\leftrightarrow - \tag{14-10}$$

(which means that a transition between a + and a − level can occur but a transition between two + levels or between two − levels cannot occur). Equation (14-9) imposes the following conditions on the total angular momentum quantum number F [see Eq. (7-47)] for the line strength not to vanish by symmetry:

$$\Delta F = 0, \pm 1 \quad (F' + F'' \geq 1). \tag{14-11}$$

The equations (14-8) and (14-11) constitute rigorous (or strict) selection rules for electric dipole transitions of an isolated molecule in field free space.

The electric dipole representation Γ^* is the same as the species in the MS group of the product $T_z\hat{J}_z$ for a symmetric top molecule [Hougen (1962c)], and is the same as the species of any of the three products $T_a\hat{J}_a$, $T_b\hat{J}_b$ or $T_c\hat{J}_c$ for an asymmetric top molecule [Hougen (1963)]. For a spherical top molecule Γ^* is the same as the species of $T_x\hat{J}_x + T_y\hat{J}_y + T_z\hat{J}_z$ [Hougen (1963)]. These results follow from the considerations of the symmetry of R_α (which has the same symmetry as $\hat{J}_\alpha$) and T_α given in Appendix 12-2.

14.1.3 Selection rules obtained after making approximations

Restrictions on the line strength are obtained by making approximations. The approximations made are those required to obtain the separable wavefunctions $\Phi_{\text{nspin}}\Phi_{\text{rot}}\Phi_{\text{vib}}\Phi_{\text{elec}}^{(e,S,m_S)}$ given by Eq. (13-1), together with the neglect of the dependence of the electronic transition moment on the nuclear coordinates, the neglect of electrical anharmonicity, and the neglect of axis switching; these three approximations are explained when they arise. As a result of these approximations selection rules are obtained that are much more restrictive than the rigorous selection rules. These restrictions involve the nuclear and electron spin, and the rotational, vibrational and electronic symmetries and quantum numbers.

To implement these approximations we must write μ_A in the expression for the line strength [Eq. (14-5)] in terms of the dipole moment components along the molecule fixed (x, y, z) axes. We could make this transformation by using direction cosine elements $\lambda_{\alpha A}$ [see Eq. (10-7)]:

$$\mu_A = \lambda_{xA}\mu_x + \lambda_{yA}\mu_y + \lambda_{zA}\mu_z, \tag{14-12}$$

and this was done in Edition 1. However, it is more convenient in the determination of the selection rules on the various angular momentum quantum numbers to transform this expression so that instead of using the Cartesian components μ_A and μ_α (where $\alpha = x$, y or z) we use the space fixed components

$$\begin{aligned} \mu_{\text{s}}^{(1,\pm1)} &= [\mp\mu_\xi + i\mu_\eta]/\sqrt{2} \\ \mu_{\text{s}}^{(1,0)} &= \mu_\zeta, \end{aligned} \tag{14-13}$$

and the molecule fixed components

$$\begin{aligned} \mu_{\text{m}}^{(1,\pm1)} &= [\mp\mu_x + i\mu_y]/\sqrt{2} \\ \mu_{\text{m}}^{(1,0)} &= \mu_z. \end{aligned} \tag{14-14}$$

The quantities $\mu_{\text{s}}^{(1,\sigma)}$ and $\mu_{\text{m}}^{(1,\sigma)}$ each transform irreducibly according to the representation $D^{(1)}$ of $\boldsymbol{K}$(spatial) [see Wigner (1959), and Tinkham (1964)], i.e., they are *irreducible spherical tensor operators* of rank 1 (see Section 10.3). The transformation properties of these operators under rotations in space are defined by the matrices $D^{(j)}(\alpha, \beta, \gamma)$ (with $j = 1$) discussed before Eq. (7-44).

These matrices have the elements $D^{(1)}_{mk}(\alpha,\beta,\gamma)$ that are related to the $|1,k,m\rangle$ functions given in Eq. (11-13). The molecule fixed axis system (x,y,z) can be viewed as a rotated version of the space fixed axis system (ξ,η,ζ), where the rotation that turns (ξ,η,ζ) into (x,y,z) is defined by the three Euler angles (ϕ, θ, χ). Consequently, we obtain the following relation between the $\mu^{(1,\sigma)}_{\mathrm{m}}$ and the $\mu^{(1,\sigma)}_{\mathrm{s}}$ [see, for example, Eq. (6.115) of Zare (1988)]

$$\mu^{(1,\sigma)}_{\mathrm{s}} = \sum_{\sigma'=-1}^{1} [D^{(1)}_{\sigma\sigma'}(\phi,\theta,\chi)]^{*}\mu^{(1,\sigma')}_{\mathrm{m}}. \tag{14-15}$$

This equation should be compared to Eq. (14-12). Equation (14-15) is a special case of the equation

$$U^{(\omega,\sigma)}_{\mathrm{s}} = \sum_{\sigma'=-\omega}^{\omega} [D^{(\omega)}_{\sigma\sigma'}(\phi,\theta,\chi)]^{*}U^{(\omega,\sigma')}_{\mathrm{m}} \tag{14-16}$$

that relates the space fixed and the molecule fixed components of an irreducible spherical tensor operator U of rank ω.

It is easily shown that in terms of the $\mu^{(1,\sigma)}_{\mathrm{s}}$ matrix elements the line strength is given by

$$S(f\leftarrow i) = \sum_{\Phi'_{\mathrm{int}},\Phi''_{\mathrm{int}}}\ \sum_{\sigma=-1}^{1} \left|\left\langle \Phi'_{\mathrm{int}} \left| \mu^{(1,\sigma)}_{\mathrm{s}} \right| \Phi''_{\mathrm{int}} \right\rangle\right|^{2}. \tag{14-17}$$

The matrix elements entering into the line strength of Eq. (14-17) can be written using separable wavefunctions as

$$\left\langle \Phi'_{\mathrm{nspin}}\Phi'_{\mathrm{rot}}\Phi'_{\mathrm{vib}}\Phi^{(e',S',m'_S)}_{\mathrm{elec}} | \mu^{(1,\sigma)}_{\mathrm{s}} | \Phi''_{\mathrm{nspin}}\Phi''_{\mathrm{rot}}\Phi''_{\mathrm{vib}}\Phi^{(e'',S'',m''_S)}_{\mathrm{elec}} \right\rangle \neq 0. \tag{14-18}$$

The dipole moment operator is independent of the nuclear spin coordinates so we can separate these variables in the integral and write it as

$$\langle \Phi'_{\mathrm{nspin}} | \Phi''_{\mathrm{nspin}} \rangle \left\langle \Phi'_{\mathrm{rot}}\Phi'_{\mathrm{vib}}\Phi^{(e',S',m'_S)}_{\mathrm{elec}} | \mu^{(1,\sigma)}_{\mathrm{s}} | \Phi''_{\mathrm{rot}}\Phi''_{\mathrm{vib}}\Phi^{(e'',S'',m''_S)}_{\mathrm{elec}} \right\rangle \neq 0. \tag{14-19}$$

We insert Eq. (14-15) in Eq. (14-19), and if we take into account the facts that $[D^{(1)}_{\sigma\sigma'}(\phi,\theta,\chi)]^{*}$ involves only the Euler angles, and that $\mu^{(1,\sigma')}_{\mathrm{m}}$ involves only the vibronic coordinates, then we can separate the rotational and vibronic parts in Eq. (14-19) to give:

$$\begin{aligned} &\langle \Phi'_{\mathrm{nspin}} | \Phi''_{\mathrm{nspin}} \rangle \sum_{\sigma'=-1}^{1} \langle \Phi'_{\mathrm{rot}} | D^{(1)*}_{\sigma\sigma'} | \Phi''_{\mathrm{rot}} \rangle \\ &\qquad \times \left\langle \Phi'_{\mathrm{vib}}\Phi^{(e',S',m'_S)}_{\mathrm{elec}} | \mu^{(1,\sigma')}_{\mathrm{m}} | \Phi''_{\mathrm{vib}}\Phi^{(e'',S'',m''_S)}_{\mathrm{elec}} \right\rangle \neq 0. \end{aligned} \tag{14-20}$$

The rotational functions Φ'_{rot} and Φ''_{rot} are linear combinations of symmetric top wavefunctions, i.e.,

$$\Phi'_{\mathrm{rot}} = \sum_{k'=-N'}^{N'} c_{k'}^{(N')} |N', k', m'\rangle , \tag{14-21}$$

with a similar equation for Φ''_{rot}. For asymmetric tops the expansion coefficients $c_k^{(N)}$ are obtained as eigenvector components from the diagonalization of the matrix representation of the asymmetric rotor Hamiltonian (see Chapter 11). For other molecules linear combinations are formed so that the Φ_{rot} functions transform irreducibly. Using Eq. (14-21) we can evaluate the rotational matrix element as

$$\langle \Phi'_{\mathrm{rot}} | D_{\sigma\sigma'}^{(1)*} | \Phi''_{\mathrm{rot}} \rangle \\ = \sum_{k'=-N'}^{N'} \sum_{k''=-N''}^{N''} c_{k'}^{(N')*} c_{k''}^{(N'')} \langle N', k', m' | D_{\sigma\sigma'}^{(1)*} | N'', k'', m'' \rangle . \tag{14-22}$$

This expression can be simplified further by means of the analytical expression [obtained, for example, from Zare (1988) using his Eq. (3.114) together with his Eqs. (3.125), (2.28), (2.30) and (2.31); note that N' and N'' are integers]

$$\langle N', k', m' | D_{\sigma\sigma'}^{(\omega)*} | N'', k'', m'' \rangle \\ = (-1)^{k'+m'} \sqrt{(2N''+1)(2N'+1)} \begin{pmatrix} N'' & \omega & N' \\ k'' & \sigma' & -k' \end{pmatrix} \begin{pmatrix} N'' & \omega & N' \\ m'' & \sigma & -m' \end{pmatrix} , \tag{14-23}$$

where here $\omega = 1$.

We can write the matrix element $\langle N', k', m' | U_{\mathrm{s}}^{(\omega,\sigma)} | N'', k'', m'' \rangle$ of an arbitrary space fixed irreducible spherical tensor operator as

$$\langle N', k', m' | U_{\mathrm{s}}^{(\omega,\sigma)} | N'', k'', m'' \rangle \\ = (-1)^{N''-m'+\omega} \begin{pmatrix} N'' & \omega & N' \\ m'' & \sigma & -m' \end{pmatrix} \langle N', k' \parallel U_{\mathrm{s}}^{(\omega)} \parallel N'', k'' \rangle . \tag{14-24}$$

This equation is the Wigner-Eckart theorem [see, for example, Eqs. (5.14) and (2.30) of Zare (1988)]. From Eqs. (14-16), (14-23), and (14-24), we can express the so-called reduced matrix element $\langle N', k' \parallel U_{\mathrm{s}}^{(\omega)} \parallel N'', k'' \rangle$ as

$$\langle N', k' \parallel U_{\mathrm{s}}^{(\omega)} \parallel N'', k'' \rangle \\ = (-1)^{N''+k'+\omega} \sqrt{(2N''+1)(2N'+1)} \sum_{\sigma'=-\omega}^{\omega} \begin{pmatrix} N'' & \omega & N' \\ k'' & \sigma' & -k' \end{pmatrix} U_{\mathrm{m}}^{(\omega,\sigma')} . \tag{14-25}$$

We can introduce a separate integration over the electronic coordinates in the vibronic matrix element of Eq. (14-20) by writing

$$\left\langle \Phi'_{\rm vib}\Phi_{\rm elec}^{(e',S',m'_S)} \left| \mu_{\rm m}^{(1,\sigma')} \right| \Phi''_{\rm vib}\Phi_{\rm elec}^{(e'',S'',m''_S)} \right\rangle = \left\langle \Phi'_{\rm vib} \left| \mu_{\rm m}^{(1,\sigma')}(e',e'') \right| \Phi''_{\rm vib} \right\rangle, \tag{14-26}$$

where the electronic integrals

$$\mu_{\rm m}^{(1,\sigma')}(e',e'') = \left\langle \Phi_{\rm elec}^{(e',S',m'_S)} \left| \mu_{\rm m}^{(1,\sigma')} \right| \Phi_{\rm elec}^{(e'',S'',m''_S)} \right\rangle, \tag{14-27}$$

called *the electronic transition moment functions*, depend on the nuclear coordinates.

By collecting the results from Eqs. (14-18)-(14-27) we obtain the following expression for the matrix elements determining the line strength:

$$\begin{aligned} \left\langle \Phi'_{\rm int} \left| \mu_{\rm s}^{(1,\sigma)} \right| \Phi''_{\rm int} \right\rangle &= \langle \Phi'_{\rm nspin} | \Phi''_{\rm nspin} \rangle \, (-1)^{m'} \sqrt{(2N''+1)(2N'+1)} \\ &\times \begin{pmatrix} N'' & 1 & N' \\ m'' & \sigma & -m' \end{pmatrix} \sum_{k'=-N'}^{N'} \sum_{k''=-N''}^{N''} (-1)^{k'} c_{k'}^{(N')*} c_{k''}^{(N'')} \\ &\times \sum_{\sigma'=-1}^{1} \left\langle \Phi'_{\rm vib} \left| \mu_{\rm m}^{(1,\sigma')}(e',e'') \right| \Phi''_{\rm vib} \right\rangle \begin{pmatrix} N'' & 1 & N' \\ k'' & \sigma' & -k' \end{pmatrix}. \end{aligned} \tag{14-28}$$

With this matrix element, we can derive an expression for the line strength using Eq. (14-17). The line strength is obtained as a sum of individual transition probabilities for all transitions between the degenerate eigenstates corresponding to the initial energy E'' and the final energy E', respectively. In the case of a completely separable wavefunction, we are concerned with three types of degeneracy:

1. The approximation of a completely separable wavefunction will only be satisfactory if we can neglect the dependence of the molecular energy on the nuclear spin functions $\Phi'_{\rm nspin}$ and $\Phi''_{\rm nspin}$. From the orthogonality of these functions it is clear that in order for the matrix element in Eq. (14-28) to be nonvanishing we must have

$$\Phi'_{\rm nspin} = \Phi''_{\rm nspin}. \tag{14-29}$$

That is

$$\Delta I = 0. \tag{14-30}$$

The spin functions are assumed to be normalized so that $\langle \Phi''_{\rm nspin} | \Phi''_{\rm nspin} \rangle = 1$. When we consider the molecular energy to be independent of $\Phi'_{\rm nspin}$ and $\Phi''_{\rm nspin}$ both the initial and the final states of the transition will be $g_{\rm ns}$-fold degenerate, where $g_{\rm ns}$ is the nuclear spin statistical weight factor discussed in Chapter 8. The summation of the transition probability over these degenerate states will, because of Eq. (14-29), introduce a factor of $g_{\rm ns}$ in the expression for the line strength.

2. The operators $\hat{\boldsymbol{S}}^2$ and $\hat{S}_Z$ commute with $\mu_{\rm m}^{(1,\sigma')}$. Consequently, the electronic integral $\mu_{\rm m}^{(1,\sigma')}(e',e'')$ in Eq. (14-27) will vanish unless $S' = S''$ and $m'_S = m''_S$. That is

   $$\Delta S = 0. \tag{14-31}$$

   The electronic integral will be independent of $m'_S = m''_S$ because the m_S quantum number describes quantization along an arbitrarily chosen space fixed direction. For the same reason the molecular energy will be independent of m_S so that both the initial and final states of the transition will be $(2S+1)$-fold degenerate. Consequently the expression for the line strength will contain this degeneracy factor.

3. The molecular energy does not depend on the quantum numbers m'' and m' [m-degeneracy]. The matrix element of Eq. (14-28), however, depends on these quantum numbers through one of the $3j$-symbols. The summation over the degeneracies in the initial and final states in Eq. (14-17) thus involves sums over m'' and m'. These sums can be evaluated together with the sum over σ in Eq. (14-17) by means of the general relation

   $$\sum_{\sigma=-\omega}^{\omega} \sum_{m''=-N''}^{N''} \sum_{m'=-N'}^{N'} \begin{pmatrix} N'' & \omega & N' \\ m'' & \sigma & -m' \end{pmatrix}^2 = 1, \tag{14-32}$$

   where $\omega = 1$ here. To obtain Eq. (14-32) we have used Eq. (2.32) of Zare (1988) in conjunction with the fact that the $3j$-symbols are real.

After having carried out the summations over the various degeneracies, we obtain the final expression for the line strength

$$\begin{aligned} S(f \leftarrow i) &= g_{\rm ns}\,(2S+1)\,(2N''+1)(2N'+1) \\ &\times \Bigg| \sum_{k'=-N'}^{N'} \sum_{k''=-N''}^{N''} c_{k'}^{(N')*}\, c_{k''}^{(N'')} \\ &\times (-1)^{k'} \sum_{\sigma'=-1}^{1} \left\langle \Phi'_{\rm vib} \left| \mu_{\rm m}^{(1,\sigma')}(e',e'') \right| \Phi''_{\rm vib} \right\rangle \begin{pmatrix} N'' & 1 & N' \\ k'' & \sigma' & -k' \end{pmatrix} \Bigg|^2 . \end{aligned} \tag{14-33}$$

This expression is valid when we take the wavefunction to be completely separable, and when we neglect the contributions to the molecular energy from electron and nuclear spin. From the general properties of the $3j$-symbol [see, for example, Zare (1988)] in Eq. (14-33), we derive that the line strength will vanish unless[4]

$$\Delta N = 0, \pm 1 \quad (N' + N'' \geq 1). \tag{14-34}$$

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[4] Remember that for a singlet state N is called J.

For an individual term in the summations of Eq. (14-33) not to vanish it must satisfy the condition $\sigma' = k' - k''$, so that the nonvanishing terms have $|k' - k''| \leq 1$. Transitions with $\Delta N = -1, 0$, and $+1$ are said to belong to the P branch, Q branch and R branch, respectively.

In obtaining Eq. (14-33), we have neglected the coupling of $\boldsymbol{N}$ to $\boldsymbol{S}$ and $\boldsymbol{I}$ described by Eqs. (10-97) and (10-99). As a result we obtain the selection rules on the angular momentum quantum numbers given by Eqs. (14-30), (14-31) and (14-34), which are more restrictive than the rigorous selection rule of Eq. (14-11).

The vibronic selection rules for completely separable wavefunctions are obtained by applying the vanishing integral rule to the vibronic matrix element $\left\langle \Phi'_{\text{vib}} \left| \mu_{\text{m}}^{(1,\sigma')}(e', e'') \right| \Phi''_{\text{vib}} \right\rangle$ in Eq. (14-33). For this matrix element to be nonvanishing we must have in the MS group

$$\Gamma''_{\text{vib}} \otimes \Gamma'_{\text{vib}} \otimes \Gamma''_{\text{elec}} \otimes \Gamma'_{\text{elec}} \supset \Gamma\left(\mu_{\text{m}}^{(1,\sigma')}\right), \tag{14-35}$$

where Γ''_{vib} and Γ'_{vib} are the respective symmetries of Φ''_{vib} and Φ'^{*}_{vib}, Γ''_{elec} and Γ'_{elec} are the respective symmetries of $\Phi_{\text{elec}}^{(e'',S'',m''_S)}$ and $\Phi_{\text{elec}}^{(e',S',m'_S)*}$, and $\Gamma\left(\mu_{\text{m}}^{(1,\sigma')}\right)$ is the symmetry of the operator $\mu_{\text{m}}^{(1,\sigma')}$. The three $\mu_{\text{m}}^{(1,\sigma')}$ do not necessarily transform irreducibly in the MS group, and in order to introduce selection rules involving the MS group labels we use the three Cartesian components μ_α; clearly the three μ_α generate the same representation of the MS group as the three $\mu_{\text{m}}^{(1,\sigma')}$. From the useful result that in the MS group

$$\Gamma(\mu_\alpha) = \Gamma(T_\alpha), \tag{14-36}$$

where T_α is a translational coordinate [see Eq. (12-147)], Eq. (14-35) can be rewritten as

$$\Gamma''_{\text{vib}} \otimes \Gamma'_{\text{vib}} \otimes \Gamma''_{\text{elec}} \otimes \Gamma'_{\text{elec}} \supset \Gamma\left(T_\alpha\right). \tag{14-37}$$

For each of the MS groups in Appendix $\boldsymbol{A}$ the species of the translational coordinates T_α are given. In order that the line strength be nonvanishing Eq. (14-37) must be satisfied for at least one of the α values x, y, or z. If k is a near quantum number that we can use to label the rotational states it follows from Eq. (14-14), and from the condition $\sigma' = k' - k'' = \Delta k$ for the individual terms in Eq. (14-33), that if Eq. (14-37) is satisfied for $\alpha = x$ or y (and not for $\alpha = z$) only transitions with $\Delta k = \pm 1$ are allowed by Eq. (14-33), whereas if Eq. (14-36) is satisfied for $\alpha = z$ (and not for $\alpha = x$ or y) then only transitions with $\Delta k = 0$ are allowed.

The three Cartesian components of the electronic transition moment function [see Eq. (14-27)] are the nuclear coordinate dependent functions

$$\mu_\alpha(e', e'') = \left\langle \Phi_{\text{elec}}^{(e',S',m'_S)} \left| \mu_\alpha \right| \Phi_{\text{elec}}^{(e'',S'',m''_S)} \right\rangle. \tag{14-38}$$

The symmetries of these functions in the MS group are

$$\Gamma\left(\mu_\alpha(e',e'')\right) = \Gamma''_{\rm elec} \otimes \Gamma'_{\rm elec} \otimes \Gamma(\mu_\alpha), \tag{14-39}$$

or, using the vanishing integral rule for Eq. (14-26) to be nonvanishing,

$$\Gamma''_{\rm vib} \otimes \Gamma'_{\rm vib} \supset \Gamma\left(\mu_\alpha(e',e'')\right). \tag{14-40}$$

Note that the vanishing integral rule is not applicable to the "partial" integral (where the integrand depends on electronic *and* nuclear coordinates, but integration is only over the electronic coordinates) in Eq. (14-38), and we do not get symmetry conditions on $\Gamma\left(\mu_\alpha(e',e'')\right)$ from the fact that Eq. (14-38) should be nonvanishing. However, in particular cases conditions can be derived from the fact that $\mu_\alpha(e',e'')$ depends on the internal nuclear coordinates (and on no other coordinates). For example, for a triatomic molecule with a bent equilibrium structure [whose MS group will be either $\boldsymbol{C}_{2v}(\mathrm{M})$ or $\boldsymbol{C}_s(\mathrm{M})$] the internal nuclear coordinates all have positive parity in that they are invariant under the feasible operation E^*. Hence any function of these coordinates also must be invariant under E^*. From this result, we can deduce that if the irreducible representation $\Gamma\left(\mu_\alpha(e',e'')\right)$ obtained from Eq. (14-39) has the character -1 under the operation E^* [that is, if the representation is either A_2 or B_1 in $\boldsymbol{C}_{2v}(\mathrm{M})$ or A'' in $\boldsymbol{C}_s(\mathrm{M})$] then $\mu_\alpha(e',e'')$ must necessarily vanish.

The function $\mu_\alpha(e',e'')$ is expressed as a Taylor expansion in the normal coordinates of one of the two electronic states involved:

$$\mu_\alpha(e',e'') = \mu_\alpha^{(0)}(e',e'') + \sum_r \mu_\alpha^{(r)}(e',e'')Q_r + \frac{1}{2}\sum_{r,s} \mu_\alpha^{(r,s)}(e',e'')Q_rQ_s + \cdots . \tag{14-41}$$

This expression is used below when we discuss further selection rules for different types of transitions. Evidently, the symmetry $\Gamma\left(\mu_\alpha(e',e'')\right)$ of $\mu_\alpha(e',e'')$ provides information about the expansion coefficients in Eq. (14-41). For example, in order that the constant term $\mu_\alpha^{(0)}(e',e'')$ can be nonvanishing, $\Gamma\left(\mu_\alpha(e',e'')\right)$ must be the totally symmetric representation of the MS group. The first derivative $\mu_\alpha^{(r)}(e',e'')$ will vanish unless $\Gamma(Q_r) = \Gamma\left(\mu_\alpha(e',e'')\right)$ [where $\Gamma(Q_r)$ is the symmetry of the normal coordinate Q_r], the second derivative $\mu_\alpha^{(r,s)}(e',e'')$ will vanish unless $\Gamma(Q_r) \otimes \Gamma(Q_s) \supset \Gamma\left(\mu_\alpha(e',e'')\right)$, and so on. For transitions between levels of different electronic states the approximation is made of neglecting all but the first term in Eq. (14-41). For transitions within one electronic state [that is, for $\Phi_{\rm elec}^{(e',S',m'_S)} = \Phi_{\rm elec}^{(e'',S'',m''_S)}$], the approximation is made of neglecting all but the first two terms in Eq. (14-41); this is termed the neglect of *electrical anharmonicity*, by analogy to the neglect of mechanical anharmonicity which is the neglect of $V_{\rm anh}$ [see Eq. (13-5)].

A transition is said to be *allowed* if its line strength is nonvanishing when calculated from Eq. (14-33) using the leading term of Eq. (14-41) for electronic transitions and the first two terms for transitions within an electronic state. If this approximate line strength vanishes, the transition is said to be *forbidden*. However, if we make fewer approximations in calculating the line strength, if we allow for axis switching, or if we consider operators other than the electric dipole moment for inducing transitions, many of the forbidden transitions will acquire nonvanishing transition probability.

Before discussing the application of these ideas to electronic, vibrational and rotational transitions we first show how the expression for the line strength [Eq. (14-33)] is changed if we introduce interactions that spoil the approximation of a separable wavefunction. The interactions we consider are rotation-vibration interaction, electron spin interaction and nuclear spin interaction. These interactions enable forbidden transitions to gain intensity.

14.1.4 Rotation-vibration interaction

If we consider transitions within one electronic state, the most important effect producing forbidden transitions is *rotation-vibration interaction*. As explained in Chapter 10, we have defined the molecular rovibrational coordinates to obtain the highest possible degree of separation between the rotational and vibrational motions [by means of the *Eckart equations* in Eq. (10-26)], but a complete separation cannot be achieved. As a result of rotation-vibration interaction, the completely separable wavefunction $\Phi_{\text{nspin}}\Phi_{\text{rot}}\Phi_{\text{vib}}\Phi_{\text{elec}}^{(e,S,m_S)}$ is replaced by $\Phi_{\text{nspin}}\Phi_{\text{rv}}\Phi_{\text{elec}}^{(e,S,m_S)}$. The form of the rotation-vibration wavefunction Φ_{rv} can be inferred from Eq. (13-217) [since we are considering one isolated electronic state here, the summation over e in Eq. (13-217) must be omitted] as:

$$\Phi_{\text{rv}} = \sum_{V,L,k} c_{eVLk}^{(N)}\, \Phi_{\text{vib}}^{(V,L)}\, |N,k,m\rangle\,. \tag{14-42}$$

In obtaining the line strength from the wavefunction involving Φ_{rv}, we can exercise all the techniques used above for the separable wavefunctions; the matrix elements between the separable wavefunctions are now matrix elements between *basis functions*, the complete wavefunction being a linear combination of these functions. When we take into account rotation-vibration interaction, the expression for the line strength from Eq. (14-33) is modified as follows

$$\begin{aligned} S(f \leftarrow i) &= g_{\text{ns}}\,(2S+1) \\ &\times \left| \sum_{V',L'} \sum_{V'',L''} \sum_{k'=-N'}^{N'} \sum_{k''=-N''}^{N''} c_{eV'L'k'}^{(N')*}\, c_{eV''L''k''}^{(N'')}\, M_{(eV''L''N''k'')}^{(eV'L'N'k')} \right|^2, \end{aligned} \tag{14-43}$$

where

$$\begin{aligned} M_{(e''V''L''N''k'')}^{(e'V'L'N'k')} &= (-1)^{N'+N''+k'} \sqrt{(2N''+1)(2N'+1)} \\ &\times \sum_{\sigma'=-1}^{1} \left\langle \Phi_{\text{vib}}^{(V',L')} \middle| \mu_{\text{m}}^{(1,\sigma')}(e',e'') \middle| \Phi_{\text{vib}}^{(V'',L'')} \right\rangle \begin{pmatrix} N'' & 1 & N' \\ k'' & \sigma' & -k' \end{pmatrix}. \end{aligned} \tag{14-44}$$

This expression for the line strength leads to selection rules less restrictive than those resulting from the simpler expression in Eq. (14-33) that was obtained for separable wavefunctions. The reason is that for the line strength in Eq. (14-33) not to vanish it is necessary that one of the three particular vibronic matrix elements $\left\langle \Phi'_{\rm vib} \middle| \mu_{\rm m}^{(1,\sigma')}(e',e'') \middle| \Phi''_{\rm vib} \right\rangle$, $\sigma' = 0, \pm 1$, satisfy Eq. (14-35) [or Eq. (14-37)]. For the line strength calculated from Eq. (14-43) not to vanish it is sufficient that one of the very many vibronic matrix elements $\left\langle \Phi_{\rm vib}^{(V',L')} \middle| \mu_{\rm m}^{(1,\sigma')}(e',e'') \middle| \Phi_{\rm vib}^{(V'',L'')} \right\rangle$ obtained by variation of σ', (V',L') and (V'',L'') satisfy conditions analogous to Eq. (14-35) or Eq. (14-37). These conditions are not all identical because the $\Phi_{\rm vib}^{(V,L)}$ functions entering into the wavefunction of Eq. (13-217) do not all have the same symmetry. The function $\Phi_{\rm rv}$ in this equation has a given symmetry $\Gamma_{\rm rv}$, and so all the products $\Phi_{\rm vib}^{(V,L)} |N,k,m\rangle$ will have this symmetry. However, for the factors in the product [namely $\Phi_{\rm vib}^{(V,L)}$ and $|N,k,m\rangle$] the only requirement is that the product of their symmetries contain $\Gamma_{\rm rv}$, and this condition will normally be fulfilled by several pairs of irreducible representations. In Section 14.1.14 we discuss the example of H_3^+ where rotational transitions (i.e., transitions within one vibrational state of one electronic state) are forbidden by Eq. (14-33) but permitted by Eq. (14-43). We note that the transitions permitted by Eq. (14-43) will satisfy Eq. (14-34), just as the transitions permitted in the approximation of separable wavefunctions.

14.1.5 Electron spin interaction

Further relaxation of the selection rules is obtained when we allow for electron spin interaction terms in the molecular Hamiltonian. In Chapter 13 we show that we can take the wavefunction $\Phi_{\rm int}$ as the product $\Phi_{\rm nspin}\Phi_{\rm rve}^{(J,m_J)}$ when we consider the effects of the electron spin in the molecular Hamiltonian. The form of $\Phi_{\rm rve}^{(J,m_J)}$ can be inferred from Eq. (13-219). In order to derive the line strength from Eq. (14-17) for such wavefunctions, we need the matrix element involving $\Phi''_{\rm nspin}\Phi_{\rm rve}^{(J'',m''_J)}$ and $\Phi'_{\rm nspin}\Phi_{\rm rve}^{(J',m'_J)}$. A substantial advantage of using irreducible spherical tensor operators $\mu_{\rm m}^{(1,\sigma')}$ and matrix elements $D_{\sigma\sigma'}^{(1)}$ [Eq. (14-15)] for expressing the line strength [instead of using the molecule fixed dipole moment components μ_α together with direction cosines such as $\lambda_{x\zeta}$, see Eq. (14-12)] is that with irreducible spherical tensor operators, we can calculate the desired matrix elements using the standard methods of angular momentum theory. Here we use the Wigner-Eckart theorem [Eq. (14-24)] to rewrite the matrix element

$$\left\langle \Phi_{\rm er}^{(e',N',S',J',k',m'_J)} \middle| \mu_{\rm s}^{(1,\sigma)} \middle| \Phi_{\rm er}^{(e'',N'',S'',J'',k'',m''_J)} \right\rangle$$
$$= (-1)^{J''-m'_J+1} \begin{pmatrix} J'' & 1 & J' \\ m''_J & \sigma & -m'_J \end{pmatrix}$$

$$\times \left\langle \Phi_{\mathrm{er}}^{(e',N',S',J',k')} \,\|\, \mu_{\mathrm{s}}^{(1)} \,\|\, \Phi_{\mathrm{er}}^{(e'',N'',S'',J'',k'')} \right\rangle . \tag{14-45}$$

The reduced matrix element can be rewritten using Eq. (5.72) of Zare (1988) as

$$\begin{aligned} &\left\langle \Phi_{\mathrm{er}}^{(e',N',S',J',k')} \,\|\, \mu_{\mathrm{s}}^{(1)} \,\|\, \Phi_{\mathrm{er}}^{(e'',N'',S'',J'',k'')} \right\rangle \\ &= \delta_{S'S''}(-1)^{N'+S''+J'+1}\sqrt{(2J''+1)(2J'+1)} \left\{ \begin{matrix} N' & J' & S' \\ J'' & N'' & 1 \end{matrix} \right\} \\ &\times \left\langle \Phi_{\mathrm{er}}^{(e',N',S',k')} \,\|\, \mu_{\mathrm{s}}^{(1)} \,\|\, \Phi_{\mathrm{er}}^{(e'',N'',S',k'')} \right\rangle , \end{aligned} \tag{14-46}$$

where the quantity in braces is a $6j$-symbol [see Eq. (10-100)]. The reduced matrix element on the right hand side of Eq. (14-46) is like that on the left hand side in Eq. (14-25), but here we must integrate over the electronic coordinates:

$$\begin{aligned} &\left\langle \Phi_{\mathrm{er}}^{(e',N',S',k')} \,\|\, \mu_{\mathrm{s}}^{(1)} \,\|\, \Phi_{\mathrm{er}}^{(e'',N'',S',k'')} \right\rangle \\ &= (-1)^{N''+k'+1}\sqrt{(2N''+1)(2N'+1)} \sum_{\sigma'=-1}^{1} \left(\begin{matrix} N'' & 1 & N' \\ k'' & \sigma' & -k' \end{matrix} \right) \\ &\times \left\langle \Phi_{\mathrm{elec}}^{(e',S',m_S)} \middle| \mu_{\mathrm{m}}^{(1,\sigma')} \middle| \Phi_{\mathrm{elec}}^{(e'',S',m_S)} \right\rangle . \end{aligned} \tag{14-47}$$

From these results the matrix elements of $\mu_{\mathrm{s}}^{(1,\sigma)}$ between the wavefunctions in Eq. (13-219) can be derived. We derive the line strength from these matrix elements in the approximation that we neglect all nuclear spin contributions to the energy, so that degeneracy will arise from the nuclear spin functions exactly as before. However, the two types of degeneracy which, for the completely separable wavefunction, were described by the m_S and m quantum numbers, are now both described by the m_J quantum number. Hence we must carry out a summation over the nuclear spin functions (which leads to a factor of g_{ns} in the expression for the line strength) and summations over m_J'' and m_J'. In these latter summations, we add the squares of the $3j$-symbol in Eq. (14-45). This sum can be evaluated from Eq. (14-32) which remains valid when we replace N, m by J, m_J. The final expression for the line strength is

$$\begin{aligned} S(f \leftarrow i) &= g_{\mathrm{ns}}(2J''+1)(2J'+1) \\ &\times \left| \sum_{S''=S'} \delta_{S''S'}(-1)^{S'} \sum_{N'=|J'-S'|}^{J'+S'} \sum_{N''=|J''-S''|}^{J''+S''} \left\{ \begin{matrix} N' & J' & S' \\ J'' & N'' & 1 \end{matrix} \right\} \right. \\ &\times \sum_{e',V',L'} \sum_{k'=-N'}^{N'} \sum_{e'',V'',L''} \sum_{k''=-N''}^{N''} M_{(e''V''L''N''k'')}^{(e'V'L'N'k')} \\ &\times \left. c_{e'V'L'S'N'k'}^{(J')*} c_{e''V''L''S''N''k''}^{(J'')} \right|^2 , \end{aligned} \tag{14-48}$$

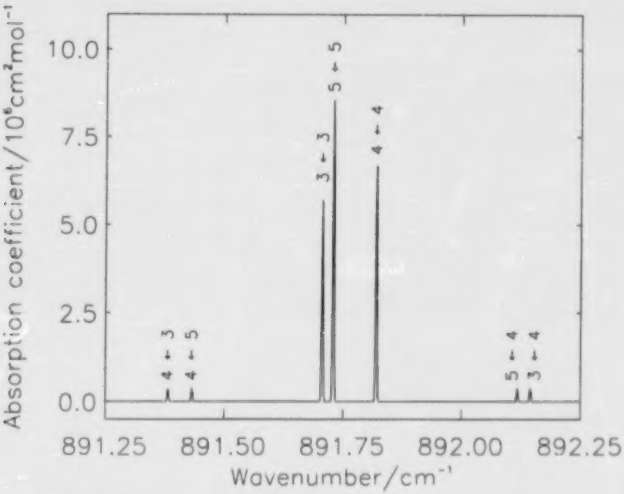

Fig. 14-1. The absorption coefficient $\epsilon(\tilde{\nu})$ [Eq. (14-1)] for the fine structure components of the $N_{K_a K_c} = 4_{04} \leftarrow 4_{13}$ transition in the ν_2 band of $\tilde{X}\,{}^3B_1$ CH_2, calculated theoretically by Kozin and Jensen (1998). It is assumed that the CH_2 molecules are in thermal equilibrium at the absolute temperature $T = 293$ K, and that the broadening of $\epsilon(\tilde{\nu})$ is caused solely by the Doppler effect [Thorne (1974)]. The theoretical calculation is based on the potential energy surface of Jensen and Bunker (1988), the dipole moment functions of Bunker and Langhoff (1983), and the spin-rotation and spin-spin interaction parameters from Kozin and Jensen (1997). The individual fine structure transitions are labeled by $J' \leftarrow J''$.

where the expansion coefficients $c^{(J)}_{eVLSNk}$ are defined in Eq. (13-219) and the quantity $M^{(e'V'L'N'k')}_{(e''V''L''N''k'')}$ is defined in Eq. (14-44). The $6j$-symbol in Eq. (14-48) vanishes unless

$$\Delta J = 0, \pm 1 \quad (J' + J'' \geq 1). \tag{14-49}$$

When electron spin effects are considered explicitly, this selection rule replaces Eq. (14-34). In principle, Eqs. (14-31) and (14-34) are now meaningless because N and S are no longer good quantum numbers. However N and S are often near quantum numbers and Eqs. (14-31) and (14-34) will be near selection rules labeling the more intense transitions.

For nonlinear molecules treated in a Hund's case (b) basis, the nonzero electron spin will cause each rotation-vibration transition to split into a number of *fine structure components* characterized by their values of $J' \leftarrow J''$. As an example of this type of splitting we show in Fig. 14-1 the fine structure components of the $N_{K_a K_c} = 4_{04} \leftarrow 4_{13}$ transition in the ν_2 band of $\tilde{X}\,{}^3B_1$ CH_2, calculated theoretically by Kozin and Jensen (1998). It is seen from the figure that the transitions with $\Delta J = \Delta N$ are much stronger than those with $\Delta J \neq \Delta N$. This is a general phenomenon. For most rotation-vibration transitions N' and N'' will both be larger than S and there will be $2S + 1$ fine structure components with $\Delta J = \Delta N$. Normally, only these lines will be observed in experimental spectra because they are much stronger than the 'satellite lines' with $\Delta J \neq \Delta N$.

14.1.6 Nuclear spin interaction

When the nuclear spin contributions [$\hat{H}_{\text{hfs}}$ in Eq. (7-23)] are explicitly accounted for the molecular wavefunctions can be taken from Eq. (13-221), and the expression for the line strength in terms of these wavefunctions is obtained from the matrix element given in Eq. (37) of Bowater, Brown, and Carrington (1973). The matrix element has been derived using the standard methods of angular momentum theory as outlined above, and the result for the line strength is

$$\begin{aligned}
S(f \leftarrow i) = (2F'' + 1)(2F' + 1) \Bigg| & \sum_{I',I''} \delta_{I'I''} \sum_{S',S''} \delta_{S'S''} (-1)^{S'+I'} \\
& \times \sum_{J'=|F'-I'|}^{F'+I'} \sum_{J''=|F''-I''|}^{F''+I''} (-1)^{J'+J''} \sqrt{(2J''+1)(2J'+1)} \\
& \times \left\{ \begin{matrix} F'' & J'' & I' \\ J' & F' & 1 \end{matrix} \right\} \sum_{N'=|J'-S'|}^{J'+S'} \sum_{N''=|J''-S''|}^{J''+S''} \left\{ \begin{matrix} J'' & N'' & S' \\ N' & J' & 1 \end{matrix} \right\} \\
& \times \sum_{e',V',L'} \sum_{k'=-N'}^{N'} \sum_{e'',V'',L''} \sum_{k''=-N''}^{N''} M^{(e'V'L'N'k')}_{(e''V''L''N''k'')} \\
& \times c^{(F')*}_{e'V'L'I'J'S'N'k'} \, c^{(F'')}_{e''V''L''I''J''S''N''k''} \Bigg|^2 ,
\end{aligned} \tag{14-50}$$

where the expansion coefficients $c^{(F)}_{eVLIJSNk}$ are defined in Eq. (13-221) and the quantity $M^{(e'V'L'N'k')}_{(e''V''L''N''k'')}$ is defined in Eq. (14-44). In obtaining Eq. (14-50), we have summed over the degeneracies associated with the m''_F and m'_F quantum numbers. The energy does not depend on m_F since it quantizes the projection of $\hat{\boldsymbol{F}}$ on an arbitrarily chosen, space fixed direction. The molecular wavefunctions Φ'_{int} and Φ''_{int} used in deriving Eq. (14-50) are eigenfunctions of $\hat{\boldsymbol{F}}^2$; they are not eigenfunctions of $\hat{\boldsymbol{N}}^2$, $\hat{\boldsymbol{S}}^2$, $\hat{\boldsymbol{J}}^2$, or $\hat{\boldsymbol{I}}^2$. Hence, in this very general approximation, the line strength will satisfy the selection rule given by Eq. (14-11), and the angular momentum quantum numbers will not be subject to any further selection rules. It is seen directly from the first 6j-symbol of Eq. (14-50) that Eq. (14-11) must be satisfied lest this symbol (and thus the entire line strength) vanish.[5]

Equation (13-247) gives the internal wavefunction describing hyperfine effects in an isolated rovibronic level of an isolated singlet electronic state. The wavefunction is obtained in the approximation that we can neglect hyperfine interaction between the rovibronic state under study and all other rovibronic states. From the expression for the internal wavefunction, we obtain the line strengths of hyperfine transitions as [see Eq. (80) of Cook and De Lucia (1971)]

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[5] See, for example, Eqs. (4.9) and (4.10) of Zare (1988).

$$S(f \leftarrow i) = \frac{S(f \leftarrow i)_{\mathrm{rve}}}{g_{\mathrm{ns}}} (2F'' + 1)(2F' + 1)$$

$$\times \left| \sum_{\mathcal{I}', I'} \sum_{\mathcal{I}'', I''} \delta_{I'I''} (-1)^{N'+I''} c^{(F')*}_{\mathcal{I}', I'} c^{(F'')}_{\mathcal{I}'', I''} \left\{ \begin{matrix} N' & F' & I'' \\ F'' & N'' & 1 \end{matrix} \right\} \right|^2 . \qquad (14\text{-}51)$$

Here $S(f \leftarrow i)_{\mathrm{rve}}$ is the line strength obtained from Eq. (14-43) in the absence of hyperfine effects; g_{ns} is the nuclear spin statistical weight factor in this equation.

The effect of nuclear spin is to make the rotation-vibration transition with line strength $S(f \leftarrow i)_{\mathrm{rve}}$ split into a number of *hyperfine components*, subject to the selection rule in Eq. (14-11). The sum of the line strengths of the hyperfine components is the line strength $S(f \leftarrow i)_{\mathrm{rve}}$ of the unsplit transition. In Fig. 14-2 we show, as an example, the hyperfine components for the $N = 15 \leftarrow 14$ rotational transition in four vibrational states (the vibrational ground state together with the ν_5^{1e}, $2\nu_5^{2e/f}$ and $3\nu_5^{3e/f}$ states) of the ^{79}BrCNO molecule [Lichau, Gillies, Gillies, Winnewisser, and Winnewisser (1997)]. The linear molecule notation used for labeling the vibrational states is analogous to that used for NCCN in Section 8.4.2 (see also Appendix 8-1), and it will be explained in Chapter 17. The ν_5 mode for BrCNO corresponds to the BrCN bend. The spectra are recorded with a BWO based millimeter spectrometer with a free space absorption cell. This experimental technique does not yield the transmittance T_{tr} [Eq. (14-2)] directly, instead the second derivative $d^2T_{\mathrm{tr}}/d\nu^2$ is obtained as a function of the frequency ν. An absorption line, which corresponds to a dip in the transmittance, thus produces a line shape function with one central, positive lobe flanked by two smaller, negative lobes. The hyperfine patterns are caused by the ^{79}Br nucleus ($I = 3/2$) and the ^{14}N nucleus ($I = 1$). ^{12}C and ^{16}O both have $I = 0$. Their widths are typically 5 MHz $\approx c \times 0.00017$ cm^{-1}. Thus the hyperfine splittings are extremely small in comparison to typical spacings between rotational levels of, say, 10-100 cm^{-1}, and typical fine structure splittings of, say, 1 cm^{-1} (see Fig. 14-1). Figure 14-2 shows that the hyperfine patterns are strongly dependent on l, the quantum number describing the projection of the rovibronic angular momentum on the axis of least moment of inertia (see Chapter 17).

Above we have derived the line strengths for electric dipole transitions using several different expressions for the molecular wavefunctions. In the crudest approximation considered here, these wavefunctions were taken to be completely separable, and the subsequent expressions for them were obtained by gradually relaxing the approximations. As discussed after Eq. (13-222), the "coupling" of the various types of molecular motion spoils successively more quantum numbers until we reach the final expression for the wavefunction given

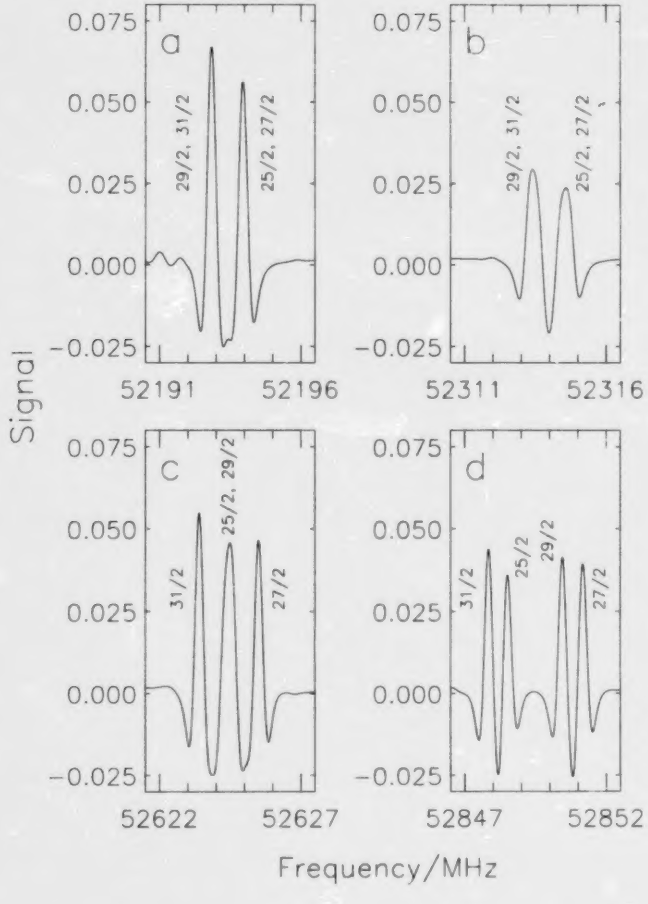

Fig. 14-2. The hyperfine components for the $N = 15 \leftarrow 14$ rotational transition of the ^{79}BrCNO molecule in a: the vibrational ground state, b: the ν_5^{1e} state, c: the $2\nu_5^{2e/f}$ state and d: the $3\nu_5^{3e/f}$ state [Lichau, Gillies, Gillies, Winnewisser, and Winnewisser (1997)]. The observed hyperfine components are labeled by their respective F''-values; they all have $\Delta F = F' - F'' = +1$. Some of the hyperfine components overlap and the corresponding peaks are labeled by two F''-values. The recorded signal is proportional to $d^2T_{\rm tr}/d\nu^2$, where ν is the frequency and the transmittance $T_{\rm tr}$ is given by Eq. (14-2).

in Eq. (13-221). In this wavefunction, all possible types of coupling are taken into account, and the line strength calculated from it will only be subject to the selection rules given by Eqs. (14-8) and (14-11). In the line strength derivations we have neglected the effects of axis switching described below.

14.1.7 Electronic transitions

We return to discussing intensities and selection rules in the simplest possible approximation, i.e., that of a completely separable wavefunction. Consequently, we assume the line strength of rovibronic transitions to be given by Eq. (14-33). When $\Phi_{\rm elec}^{(e',S',m_S')} \neq \Phi_{\rm elec}^{(e'',S'',m_S'')}$, a vibronic band will be allowed if $\Gamma''_{\rm vib}$, $\Gamma'_{\rm vib}$, $\Gamma''_{\rm elec}$ and $\Gamma'_{\rm elec}$ satisfy Eq. (14-37). The strongest transitions of this type are *electronically allowed* in that they further satisfy

$$\Gamma'_{\rm elec} \otimes \Gamma''_{\rm elec} \supset \Gamma(\mu_\alpha) = \Gamma(T_\alpha) \tag{14-52}$$

and

$$\Gamma'_{\rm vib} = \Gamma''_{\rm vib}. \tag{14-53}$$

These transitions are generally strong because when Eq. (14-52) is satisfied, the constant term $\mu_\alpha^{(0)}(e', e'')$ in Eq. (14-41) is nonvanishing. This term normally contributes much more to the vibronic matrix elements $\langle \Phi'_{\rm vib} \, | \mu_\alpha(e', e'') | \, \Phi''_{\rm vib} \rangle$ than the subsequent, higher-order terms depending on the normal coordinates. The electronically allowed transitions are such that the species of the electronic wavefunctions in the MS group[6] must be connected by a translation. Further the vibrational states involved in the transition must belong to the same symmetry species in the MS group. For an absorption transition from the vibronic ground state of a molecule the vibrational ground state wavefunction is totally symmetric so that only totally symmetric vibrations of the upper electronic state can be excited by electronically allowed transitions.

In estimating the intensities of electronically allowed transitions we truncate the expansion in Eq. (14-41) after the constant term $\mu_\alpha^{(0)}(e', e'')$. In this approximation, the vibronic matrix element

$$|\langle \Phi'_{\rm vib} \, | \mu_\alpha(e', e'') | \, \Phi''_{\rm vib} \rangle|^2 = \left| \mu_\alpha^{(0)}(e', e'') \right|^2 \, |\langle \Phi'_{\rm vib} | \Phi''_{\rm vib} \rangle|^2 \tag{14-54}$$

involves the *Franck-Condon factor* $|\langle \Phi'_{\rm vib} | \Phi''_{\rm vib} \rangle|^2$, which is the square of the overlap integral between the initial and final vibrational wavefunctions. The Franck-Condon factors give the relative intensities of the vibronic bands within an electronic band system. This is referred to as the *Franck-Condon principle*. If the equilibrium geometries of the two electronic states involved in the transition are significantly different then the Franck-Condon principle results in the occurrence of long vibrational progressions [see, for example, Herzberg (1989) pages 193-204, and Herzberg (1991b) pages 142-150].

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[6] The MS group is that appropriate for the simultaneous treatment of the electronic states under consideration.

Electronically forbidden transitions [i.e., transitions for which Eqs. (14-52) and (14-53) are not fulfilled] can still be *vibronically allowed* because they satisfy Eq. (14-37). If we define $\Gamma_{\mathrm{ve}} = \Gamma_{\mathrm{vib}} \otimes \Gamma_{\mathrm{elec}}$, we can reformulate Eq. (14-37) as

$$\Gamma'_{\mathrm{ve}} \otimes \Gamma''_{\mathrm{ve}} \supset \Gamma(\mu_\alpha) = \Gamma(T_\alpha), \tag{14-55}$$

where $\alpha = x, y$, or z. Such a vibronically allowed transition can have appreciable intensity if the electronic transition moment $\mu_\alpha(e', e'')$ depends strongly on the nuclear coordinates, in which case the terms of first and higher order in the normal coordinates in Eq. (14-41) will have significant magnitude.

A vibronically allowed (but electronically forbidden) transition can also acquire intensity from vibronic or rovibronic interactions. If we neglect spin effects then the internal molecular wavefunction is given by Eq. (13-217). We consider a transition to an electronic state e_i which is coupled to another electronic state e_j by vibronic and/or rovibronic interactions. If we neglect the coupling of the two states to all other electronic states we can use Eq. (13-217) to express the internal wavefunctions as

$$\begin{aligned}\Phi'_{\mathrm{int}} = \Phi'_{\mathrm{nspin}} \Bigg[& \Phi_{\mathrm{elec}}^{(e_i,S,m_S)} \sum_{V_i,L_i,k_i} c_{e_iV_iL_ik_i}\, \Phi_{\mathrm{rv}}^{(V_i,L_i,N,k_i,m)} \\ & + \Phi_{\mathrm{elec}}^{(e_j,S,m_S)} \sum_{V_j,L_j,k_j} c_{e_jV_jL_jk_j}\, \Phi_{\mathrm{rv}}^{(V_j,L_j,N,k_j,m)} \Bigg] \\ = {} & \Phi'_{\mathrm{nspin}} \left[\Phi_{\mathrm{elec}}^{(e_i,S,m_S)} \Phi_{\mathrm{rv}}^{(i)} + \Phi_{\mathrm{elec}}^{(e_j,S,m_S)} \Phi_{\mathrm{rv}}^{(j)} \right],\end{aligned} \tag{14-56}$$

where the rotation-vibration wavefunctions $\Phi_{\mathrm{rv}}^{(i)}$ and $\Phi_{\mathrm{rv}}^{(j)}$ serve as coefficients of the electronic wavefunctions in the expression for the internal wavefunction. The wavefunctions $\Phi_{\mathrm{rv}}^{(i)}$ and $\Phi_{\mathrm{rv}}^{(j)}$ are not individually normalized but satisfy

$$\left| \left\langle \Phi_{\mathrm{rv}}^{(i)} | \Phi_{\mathrm{rv}}^{(i)} \right\rangle \right|^2 + \left| \left\langle \Phi_{\mathrm{rv}}^{(j)} | \Phi_{\mathrm{rv}}^{(j)} \right\rangle \right|^2 = 1$$

so that Φ'_{int} is normalized. We consider rovibronic transitions to the interacting e_i/e_j electronic states from an isolated electronic state e'' for which the internal wavefunctions can be written as

$$\Phi''_{\mathrm{int}} = \Phi''_{\mathrm{nspin}} \Phi_{\mathrm{elec}}^{(e'',S,m_S)} \Phi''_{\mathrm{rv}}. \tag{14-57}$$

The intensities of the rovibronic transitions are determined by the matrix elements

$$\begin{aligned}\left\langle \Phi'_{\mathrm{int}} \left| \mu_{\mathrm{s}}^{(1,\sigma)} \right| \Phi''_{\mathrm{int}} \right\rangle = {} & \left\langle \Phi_{\mathrm{elec}}^{(e_i,S,m_S)} \Phi_{\mathrm{rv}}^{(i)} \left| \mu_{\mathrm{s}}^{(1,\sigma)} \right| \Phi_{\mathrm{elec}}^{(e'',S,m_S)} \Phi''_{\mathrm{rv}} \right\rangle \\ & + \left\langle \Phi_{\mathrm{elec}}^{(e_j,S,m_S)} \Phi_{\mathrm{rv}}^{(j)} \left| \mu_{\mathrm{s}}^{(1,\sigma)} \right| \Phi_{\mathrm{elec}}^{(e'',S,m_S)} \Phi''_{\mathrm{rv}} \right\rangle,\end{aligned} \tag{14-58}$$

where the operator $\mu_{\mathrm{s}}^{(1,\sigma)}$ is defined in Eq. (14-13) and we have used Eq. (14-29). Each of the two matrix elements on the right hand side of Eq. (14-58) can be determined by using the techniques leading to Eq. (14-43).

We assume that the rovibronic states in the electronic state e_i are only weakly perturbed by those of e_j; this means that

$$\left|\left\langle\Phi_{\mathrm{rv}}^{(i)}|\Phi_{\mathrm{rv}}^{(i)}\right\rangle\right|^2 \gg \left|\left\langle\Phi_{\mathrm{rv}}^{(j)}|\Phi_{\mathrm{rv}}^{(j)}\right\rangle\right|^2 .$$

In this event, it is natural to say that the rovibronic transitions with intensities described by Eq. (14-58) belong to the electronic transition $e_i \leftarrow e''$. However, if this transition is electronically forbidden, whereas the electronic transition $e_j \leftarrow e''$ is electronically allowed, the dominant contribution to the intensities of these rovibronic transitions normally originates in the second matrix element on the right hand side of Eq. (14-58). This matrix element formally describes the intensity of a rovibronic transition in the $e_j \leftarrow e''$ electronic band system, and we say that the electronically forbidden transition $e_i \leftarrow e''$ ***steals*** (or ***borrows***) intensity from the electronically allowed transition $e_j \leftarrow e''$.

The effect of ***intensity stealing*** (or ***intensity borrowing***) is often observed in experimental spectra. When interactions are considered explicitly the internal wavefunctions are linear combinations of many basis functions, each of which is a completely separable wavefunction. When line strengths are calculated from the internal wavefunctions some of the basis functions will provide nonvanishing vibronic matrix elements, and some of them will not. States that provide nonvanishing vibronic matrix elements are called ***bright states***, those that do not are ***dark states***. As a result of intensity stealing (weak) transitions to states with wavefunctions predominantly made up of dark basis states can often be observed. In the event that the mixing of bright and dark basis states is caused by accidental resonances (or accidental degeneracies, i.e., situations where two zero order rovibronic energies associated with completely separable basis functions happen to be close), intensity stealing can cause great irregularities in the observed spectra.

14.1.8 Axis switching

If the equilibrium geometries of the two electronic states $\Phi_{\mathrm{elec}}^{(e',S',m_S')}$ and $\Phi_{\mathrm{elec}}^{(e'',S'',m_S'')}$ are different then the molecule fixed (x,y,z) axes would be differently oriented in the two states for a given instantaneous nuclear arrangement. This is because the orientation of the axes is determined by using the Eckart conditions and the equilibrium geometry enters into these [see Eqs. (10-27)-(10-37)]. This effect is called ***axis switching*** [Hougen and Watson (1965)]. As a result we must choose the equilibrium configuration of one of the electronic states as *the* equilibrium geometry to use in the Eckart equations in order to define uniquely a set of (x,y,z) axes so that the Euler angles (θ,ϕ,χ) and the molecule fixed dipole moment components μ_α [which, in turn, determine the $[D_{\sigma\sigma'}^{(1)}(\phi,\theta,\chi)]^*$ functions and the $\mu_{\mathrm{m}}^{(1,\sigma')}$ operators in Eq. (14-16)] can be unambiguously determined. The rotational wavefunctions of the other electronic state would then have to be written in terms of rotational wavefunctions that are functions of Euler angles defined by these new axes in order that the rotational matrix elements of $[D^{(1)}_{\sigma\sigma'}(\phi, \theta, \chi)]^*$ involve only one set of angles. The result of this would be that certain "extra" rotational transitions called axis switching transitions would become allowed, and they do not obey the selection rules on K (or K_a and K_c) that we derive below. This effect would also need to be considered in the comparison of *ab initio* and experimental vibronic matrix elements of μ_α. Axis switching transitions are not of common occurrence and are generally weak.

14.1.9 The Herzberg-Teller effect

We have seen that an electronically forbidden (but vibronically allowed) transition can gain observable intensity if the electronic transition moment $\mu_\alpha(e', e'')$ depends strongly on the nuclear coordinates or if the transition steals intensity from another (electronically allowed) transition. These effects were first discussed by Herzberg and Teller (1933), and intensities induced by the dependence of $\mu_\alpha(e', e'')$ on the nuclear coordinates or by intensity stealing resulting from *vibronic* interaction [see also Sharf (Scharf) (1971), and Orlandi and Siebrand (1972)], are said to be caused by the *Herzberg-Teller effect*.

The 2600 Å absorption system of benzene, studied by Callomon, Dunn, and Mills (1966), exhibits the Herzberg-Teller effect. Figure 14-3 shows a low-resolution spectrum of C_6H_6 between 37000 and 43000 cm^{-1}. In both the upper and the lower electronic state of the transition, the equilibrium structure of the benzene molecule has $\boldsymbol{D}_{6h}$ point group symmetry, therefore the appropriate molecular symmetry group for describing the transition is $\boldsymbol{D}_{6h}(M)$ [see Table A-11]. The lower electronic state is the ground state of A_{1g} symmetry in $\boldsymbol{D}_{6h}(M)$; the upper electronic state has B_{2u} symmetry. The translational coordinates of benzene have the symmetries $\Gamma(T_x, T_y) = E_{1u}$ and $\Gamma(T_z) = A_{2u}$, so Eq. (14-52) is not satisfied by the electronic symmetries $\Gamma'_{elec} = B_{2u}$ and $\Gamma''_{elec} = A_{1g}$; the transition is electronically forbidden. However, Fig. 14-3 shows that vibronically allowed absorption bands occur in the spectrum. The most prominent progression of bands are labeled A in the figure; the band A^0_n is a vibronic transition from the vibrational ground state of the electronic ground state to the $(n\nu_1 + \nu_6)'$ vibrational state of the excited electronic state. The ν_1 vibrational mode has A_{1g} symmetry, and ν_6 has E_{2g} symmetry in both electronic states. Thus all of the bands in the A progression satisfy Eq. (14-55). Figure 14-4 is a vibronic energy level diagram that identifies the bands labeled in Fig. 14-3. The ν_7 vibrational mode, which also gives rise to a vibronically allowed transition, has E_{2g} symmetry. In Fig. 14-4 we also label the transition from the $v''_j\nu_j$ vibrational state in the lower electronic state to the $v'_j\nu_j$ vibrational state in the upper electronic state using the standard notation $j^{v'_j}_{v''_j}$.

We have described two apparently different causes for the Herzberg-Teller effect: the strong dependence of the electronic transition moment $\mu_\alpha(e', e'')$ on the nuclear coordinates, or an intensity stealing that results from vibronic interaction. In fact these are simply two different ways of describing the same

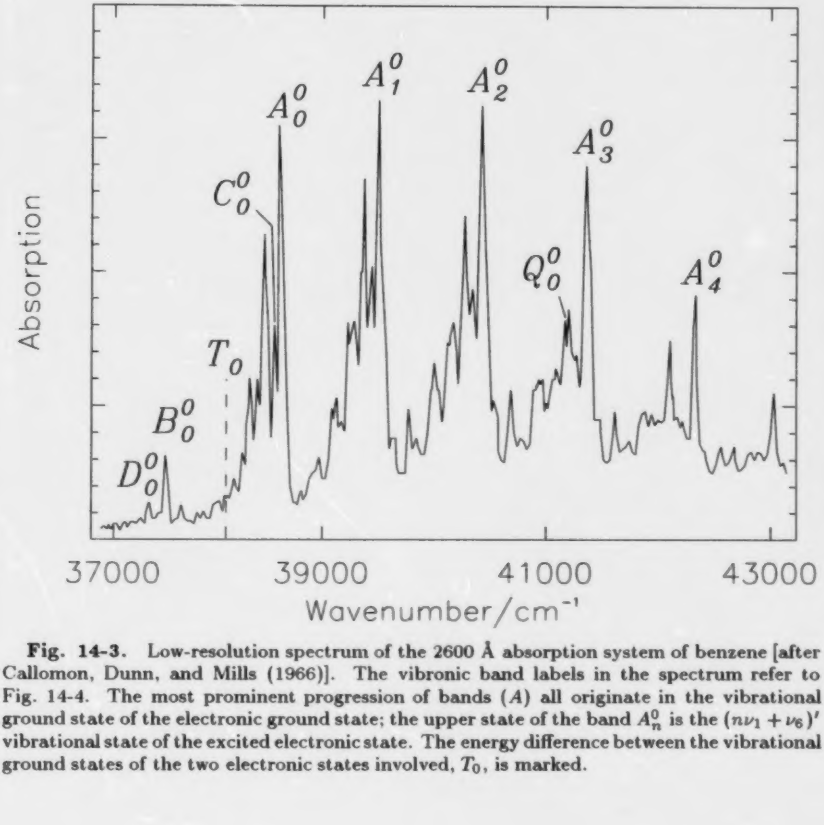

Fig. 14-3. Low-resolution spectrum of the 2600 Å absorption system of benzene [after Callomon, Dunn, and Mills (1966)]. The vibronic band labels in the spectrum refer to Fig. 14-4. The most prominent progression of bands (A) all originate in the vibrational ground state of the electronic ground state; the upper state of the band A_n^0 is the $(n\nu_1 + \nu_6)'$ vibrational state of the excited electronic state. The energy difference between the vibrational ground states of the two electronic states involved, T_0, is marked.

physical effect, and we explain this following a line of reasoning suggested to us by Prof. I. M. Mills. Consider initially the particular nuclear geometry in which all normal coordinates $Q_r = 0$; this will be the equilibrium geometry of one of the electronic states under study. The electronic wavefunctions obtained at this nuclear geometry (which depend on the electronic coordinates) are denoted $\Phi_{\text{elec}}^{(e'',S,m_S)}(0)$, $\Phi_{\text{elec}}^{(e_i,S,m_S)}(0)$, $\Phi_{\text{elec}}^{(e_j,S,m_S)}(0)$, ..., where the ... indicate other electronic states. Let one normal coordinate, Q_t say, be different from zero. In the displaced geometry we solve the electronic Schrödinger equation by diagonalizing a matrix representation of the electronic Hamiltonian $\hat{H}_{\text{elec}}$ in the basis set $\Phi_{\text{elec}}^{(e'',S,m_S)}(0)$, $\Phi_{\text{elec}}^{(e_i,S,m_S)}(0)$, $\Phi_{\text{elec}}^{(e_j,S,m_S)}(0)$, ... The electronic wavefunctions at the displaced geometry are expressed as linear combinations of the basis functions, and we assume that at the displaced geometry $\Phi_{\text{elec}}^{(e_i,S,m_S)}$

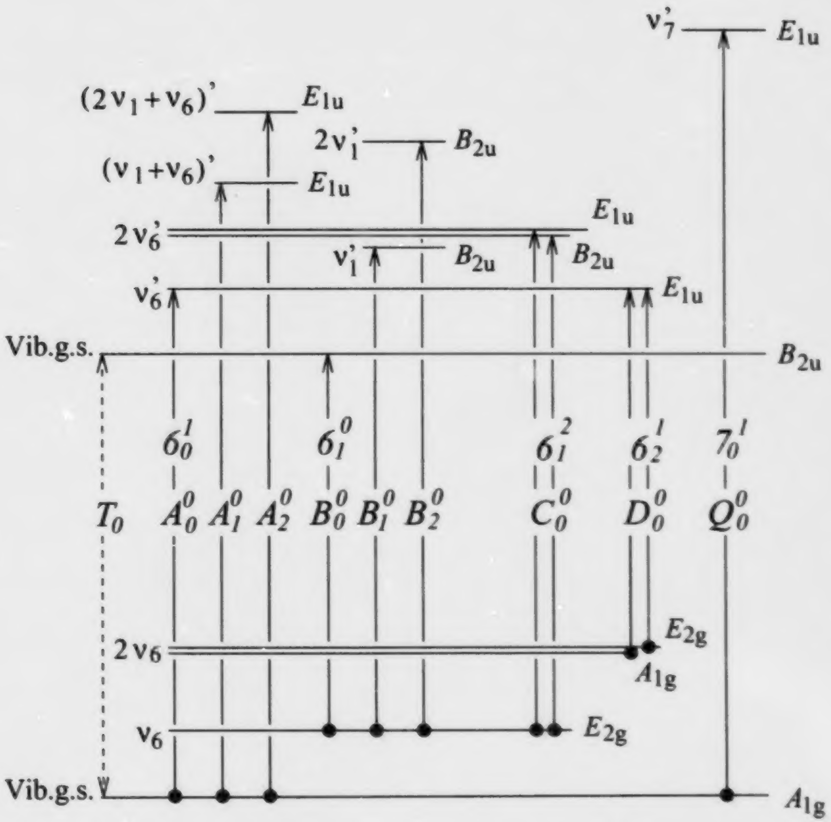
ν'₇
E₁ᵤ
(2ν₁+ν₆)'
E₁ᵤ
2ν'₁
B₂ᵤ
(ν₁+ν₆)'
E₁ᵤ
E₁ᵤ
2ν'₆
ν'₁
B₂ᵤ
B₂ᵤ
ν'₆
E₁ᵤ
Vib.g.s.
B₂ᵤ
6¹₀
6⁰₁
6²₁
6¹₂
7¹₀
T₀
A⁰₀
A⁰₁
A⁰₂
B⁰₀
B⁰₁
B⁰₂
C⁰₀
D⁰₀
Q⁰₀
2ν₆
E₂g
A₁g
ν₆
E₂g
Vib.g.s.
A₁g

Fig. 14-4. Basic vibronic energy level diagram for the 2600 Å absorption system of benzene [after Callomon, Dunn, and Mills (1966)]. For each vibronic state we give on the left the quantum number labels and on the right the vibronic symmetry $\Gamma_{\rm ve}$. The vibronic transitions indicated all satisfy Eq. (14-55). The vibronic band labels refer to Fig. 14-3.

is given by

$$\begin{aligned}\Phi_{\rm elec}^{(e_i,S,m_S)}(Q_r) &\approx c_i^{(i)}\,\Phi_{\rm elec}^{(e_i,S,m_S)}(0) + c_j^{(i)}\,\Phi_{\rm elec}^{(e_j,S,m_S)}(0)\\ &\approx c_i^{(i)}\,\Phi_{\rm elec}^{(e_i,S,m_S)}(0) + C_{j,t}^{(i)}\,Q_t\,\Phi_{\rm elec}^{(e_j,S,m_S)}(0), \qquad (14\text{-}59)\end{aligned}$$

i.e., that we can neglect all contributions except those from $\Phi_{\rm elec}^{(e_i,S,m_S)}(0)$ and $\Phi_{\rm elec}^{(e_j,S,m_S)}(0)$. In Eq. (14-59) the expansion coefficient $|c_i^{(i)}| \approx 1$ and $|c_j^{(i)}| \ll 1$ (since we are considering a geometry only slightly displaced from that with all $Q_r = 0$). Further, the coefficient $c_j^{(i)}$ must vanish when $Q_t = 0$ and in a first approximation we can take it to be proportional to Q_t with the proportionality constant $C_{j,t}^{(i)}$ as indicated in Eq. (14-59). For $C_{j,t}^{(i)}$ to be nonvanishing we must have

$$\Gamma_{\text{elec}}^{(i)} \otimes \Gamma_{\text{elec}}^{(j)} \supset \Gamma(Q_t), \tag{14-60}$$

where $\Gamma_{\text{elec}}^{(i)}$ and $\Gamma_{\text{elec}}^{(j)}$ are the MS group symmetries of $\Phi_{\text{elec}}^{(e_i,S,m_S)}$ and $\Phi_{\text{elec}}^{(e_j,S,m_S)}$ respectively, and $\Gamma(Q_t)$ is the MS group symmetry of Q_t. Comparison of Eqs. (13-155) and (14-60) shows that the mixing described by Eq. (14-59) takes place between electronic states that can be coupled by the vibronic interaction caused by H_1 in Eq. (13-150).

For simplicity we assume that the electronic wavefunction $\Phi_{\text{elec}}^{(e'',S,m_S)}$, which for an absorption transition would be the electronic ground state, is not appreciably mixed with other electronic states at the displaced geometry so that

$$\Phi_{\text{elec}}^{(e'',S,m_S)}(Q_r) \approx \Phi_{\text{elec}}^{(e'',S,m_S)}(0). \tag{14-61}$$

From the wavefunctions in Eqs. (14-59) and (14-61), we obtain the electronic transition moment [Eq. (14-38)] at the displaced geometry as

$$\begin{aligned}\mu_\alpha(e_i, e'') = {} & c_i^{(i)} \left\langle \Phi_{\text{elec}}^{(e_i,S,m_S)}(0) \,|\mu_\alpha|\, \Phi_{\text{elec}}^{(e'',S,m_S)}(0) \right\rangle \\ & + C_{j,t}^{(i)} Q_t \left\langle \Phi_{\text{elec}}^{(e_j,S,m_S)}(0) \,|\mu_\alpha|\, \Phi_{\text{elec}}^{(e'',S,m_S)}(0) \right\rangle ,\end{aligned} \tag{14-62}$$

where the electronic integrals are calculated at the geometry with all $Q_r = 0$. The first matrix element on the right hand side of Eq. (14-62) vanishes because the transition $e_i \leftarrow e''$ is electronically forbidden, but the second matrix element is nonvanishing. Comparison of Eqs. (14-41) and (14-62) shows that

$$\mu_\alpha^{(t)}(e_i, e'') = C_{j,t}^{(i)} \left\langle \Phi_{\text{elec}}^{(e_j,S,m_S)}(0) \,|\mu_\alpha|\, \Phi_{\text{elec}}^{(e'',S,m_S)}(0) \right\rangle . \tag{14-63}$$

The parameter $\mu_\alpha^{(t)}(e_i, e'')$ will have a large absolute value if $|C_{j,t}^{(i)}|$ is large. This will be the case if displacement of the nuclei leads to strong mixing of the electronic states, i.e., if there is strong vibronic interaction. In general, the electronic transition moment $\mu_\alpha(e', e'')$ is strongly dependent on the nuclear coordinates if there is strong vibronic interaction and vice versa. Consequently the two apparently different causes for the Herzberg-Teller effect discussed above are in fact two different manifestations of the same phenomenon.

Recent examples of work involving the Herzberg-Teller effect include a theoretical study of the resonance Raman spectrum of cyclobutene [Negri, Orlandi, Zerbetto, and Zgierski (1995)] and an experimental and theoretical study of an electronic spectrum of CS$_2$ [Cossart-Magos, Horani, Jungen, and Launay (1996)]. Rotationally resolved spectra of high overtones of the intermoiety stretching vibration in the benzene-argon complex have been measured by Neuhauser, Braun, Neusser and van der Avoird (1998) using the technique of coherent ion dip spectroscopy. Herzberg-Teller coupling in the benzene chromophore, induced by the ν_6 vibrational mode in the excited electronic state (as described above), makes it possible to use the 6^1 level of the excited electronic state as the upper state in the laser pumping stage of this excitation.[7] In addition to the vibronic effects included in the Herzberg-Teller effect rovibronic interaction can also cause intensity stealing and make electronically forbidden transitions allowed.

14.1.10 The Renner effect

The Renner effect (see Section 13.4.1) is a rovibronic interaction between two electronic states. If we name the two states e_i and e_j then the internal wavefunction associated with each of them can be expressed as in Eq. (14-56). For rovibronic transitions within the two electronic states coupled by the Renner interaction the line strength is determined by the matrix element

$$\begin{aligned}\left\langle \Phi'_{\rm int} \left| \mu_{\rm s}^{(1,\sigma)} \right| \Phi''_{\rm int} \right\rangle = {} & \left\langle \Phi_{\rm elec}^{(e_i,S,m_S)} \Phi_{\rm rv}^{(i)\prime} \left| \mu_{\rm s}^{(1,\sigma)} \right| \Phi_{\rm elec}^{(e_i,S,m_S)} \Phi_{\rm rv}^{(i)\prime\prime} \right\rangle \\ & + \left\langle \Phi_{\rm elec}^{(e_j,S,m_S)} \Phi_{\rm rv}^{(j)\prime} \left| \mu_{\rm s}^{(1,\sigma)} \right| \Phi_{\rm elec}^{(e_j,S,m_S)} \Phi_{\rm rv}^{(j)\prime\prime} \right\rangle \\ & + \left\langle \Phi_{\rm elec}^{(e_i,S,m_S)} \Phi_{\rm rv}^{(i)\prime} \left| \mu_{\rm s}^{(1,\sigma)} \right| \Phi_{\rm elec}^{(e_j,S,m_S)} \Phi_{\rm rv}^{(j)\prime\prime} \right\rangle \\ & + \left\langle \Phi_{\rm elec}^{(e_j,S,m_S)} \Phi_{\rm rv}^{(j)\prime} \left| \mu_{\rm s}^{(1,\sigma)} \right| \Phi_{\rm elec}^{(e_i,S,m_S)} \Phi_{\rm rv}^{(i)\prime\prime} \right\rangle , \end{aligned} \qquad (14\text{-}64)$$

where the operator $\mu_{\rm s}^{(1,\sigma)}$ is defined in Eq. (14-13) and we have used Eq. (14-29). In Eq. (14-64) we have added prime and double prime labels to the rotation-vibration wavefunctions in order to identify the initial ($''$) and final ($'$) states. Each of the four matrix elements on the right hand side of Eq. (14-64) can be determined by using the techniques leading to Eq. (14-43).

In connection with Eqs. (14-38) and (14-39) above we mentioned that for a triatomic molecule a nonvanishing function $\mu_\alpha(e', e'')$ transforms according to the irreducible representation A_1 or B_2 if the MS group of the molecule is $\boldsymbol{C}_{2v}$(M) (i.e., if the molecule is of type ABA), and according to A' if the MS group is $\boldsymbol{C}_s$(M). We also know from Section 13.4.1 that the symmetries $\Gamma_{\rm elec}^{(i)}$ and $\Gamma_{\rm elec}^{(j)}$ of the two electronic states coupled by the Renner effect are such that $\Gamma_{\rm elec}^{(i)} \otimes \Gamma_{\rm elec}^{(j)}$ is B_1 for $\boldsymbol{C}_{2v}$ molecules, and A'' for $\boldsymbol{C}_s$ molecules. The molecule fixed axes of a triatomic molecule are normally defined with a $\mathrm{I^r}$ convention (see discussion after Fig. 10-2 on page 210) so that the axis perpendicular to the molecular plane (which is necessarily the c axis) is labeled y; the x and z axes are in-plane. With these definitions we can use the symmetry information summarized above to show that the five functions $\mu_x(e_i, e_i)$, $\mu_z(e_i, e_i)$, $\mu_x(e_j, e_j)$, $\mu_z(e_j, e_j)$ and $\mu_y(e_i, e_j)$ are nonvanishing [see also Osmann, Bunker, Jensen, and Kraemer (1997)]. If, for a $\boldsymbol{C}_{2v}$ molecule, the molecule fixed axes (x, y, z) are oriented as shown for the H_2O molecule in Fig. 10-2, then $\mu_x(e_i, e_i)$, $\mu_x(e_j, e_j)$ and $\mu_y(e_i, e_j)$ all have A_1 symmetry whereas $\mu_z(e_i, e_i)$ and $\mu_z(e_j, e_j)$ have B_2 symmetry. For a $\boldsymbol{C}_s$ molecule all five functions have A' symmetry.

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[7] These authors use the notation $PI(C_{6v})$ for what we call $\boldsymbol{C}_{6v}$(M).

The two functions $\mu_x(e_i, e_i)$ and $\mu_z(e_i, e_i)$ determine the first matrix element (which can be thought of as describing a rotation-vibration transition within the e_i electronic state) on the right hand side of Eq. (14-64), and the two functions $\mu_x(e_j, e_j)$ and $\mu_z(e_j, e_j)$ determine the second matrix element (which can be thought of as describing a rotation-vibration transition within the e_j electronic state). The function $\mu_y(e_i, e_j)$ determines the last two matrix elements, which can be thought of as describing rovibronic transitions between the e_i and e_j states. There is obviously ample opportunity for intensity stealing between $e_i \leftarrow e_i$, $e_j \leftarrow e_j$ and $e_i \leftrightarrow e_j$ transitions. The details of the Renner interaction, and thus the details of the intensity stealing, are strongly dependent on the exact structure of the bending potentials in the two interacting electronic states (see Fig. 13-6 on page 372).

As an example we consider the $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ electronic states of CH_2 (see Fig. 13-7 on page 374 and Fig. 13-14 on page 398), which become degenerate as a $^1\Delta_g$ state at linearity. The barrier to linearity in the $\tilde{a}$ state is close to 9000 cm^{-1}, and that in the $\tilde{b}$ state is close to 1000 cm^{-1}. Hence, the $\tilde{a}$ rovibronic states significantly below the $\tilde{a}$-state barrier are relatively unperturbed by the Renner effect; this energy region of the $\tilde{a}$ state has been the subject of several experimental studies (see Hartland, Qin, and Dai (1995) and references therein). In the energy region above the $\tilde{a}$-state barrier vibronic transitions have also been observed, starting with the classic work of Herzberg and Johns (1966) [see also Petek, Nesbitt, Darwin, and Moore (1987), Green, Chen, Bitto, Guyer, and Moore (1989), and Chang, Wu, Hall, and Sears (1994)]. A summary of the data measured in this region prior to 1991 is given in Tables V-IX of Green, Handy, Knowles, and Carter (1991). For transitions starting in the $\tilde{a}$ vibrational ground state and ending in a state above the $\tilde{a}$ barrier to linearity, the dominant source of intensity is the vibronic transition moment of the $\tilde{b} \leftarrow \tilde{a}$ transition. However, as seen in Tables VI-IX of Green, Handy, Knowles, and Carter (1991), the experimental results include several transitions from the $\tilde{a}$ vibrational ground state to rovibronic states with $K_a > 0$ which, according to the theoretical calculations of these authors, belong predominantly to the $\tilde{a}$ electronic state. These transitions steal intensity from the $\tilde{b} \leftarrow \tilde{a}$ electronic transition by means of the mechanism expressed in Eq. (14-64).

14.1.11 The Jahn-Teller effect

For a rovibronic transition within a doubly degenerate electronic state subject to the Jahn-Teller effect the intensity can be expressed in terms of the matrix element given by Eq. (14-64) if we take e_i and e_j to be the two components of the electronic state. Again, intensity stealing can take place between the transitions within the two electronic components and the transitions connecting them. As mentioned above the detailed effects of Renner interaction between electronic states will depend on the details of the Born-Oppenheimer potential energy functions involved, and so it is impossible to give a general description of the phenomenon. In the case of Jahn-Teller interaction, the zero order model is always that of the two degenerate, near-harmonic electronic states at a high-symmetry nuclear configuration and it is easier to give a general treatment. The intensities of rovibronic absorption transitions in Jahn-Teller degenerate electronic states were discussed first by Child and Longuet-Higgins (1961), and extensions of their work have been made by Scharf and Miller (1986) and by Watson (1986).

For a doubly degenerate electronic state with MS group symmetry Γ_{elec} the electronic matrix elements $\mu_\alpha(e_i, e_i)$, $\mu_\alpha(e_j, e_j)$ and $\mu_\alpha(e_i, e_j)$ $[\alpha = x, y, z]$ will transform according to the MS group representation

$$\Gamma(\boldsymbol{\mu}) = \Gamma(\boldsymbol{T}) \otimes [\Gamma_{\text{elec}}]^2, \tag{14-65}$$

where $\Gamma(\boldsymbol{T})$ is a shorthand notation for the MS group symmetry spanned by the translational coordinates (T_x, T_y, T_z), and $[\Gamma_{\text{elec}}]^2$ indicates the symmetric product representation [see Eq. (6-119)]. Equation (14-65) is the degenerate-electronic-state version of Eq. (14-39).

For example, if we consider a molecule with the MS group $\boldsymbol{D}_{3h}(\text{M})$ [Table A-10], in an electronic state of symmetry E' or E'', we obtain

$$\Gamma(\boldsymbol{\mu}) = A_1' \oplus A_2' \oplus A_2'' \oplus 2E' \oplus E''. \tag{14-66}$$

Since $\Gamma(\boldsymbol{\mu})$ contains the totally symmetric representation A_1', the condition for the molecule to have a pure rotational spectrum [see Eqs. (14-84) and (14-85)] is fulfilled. Closer inspection shows this spectrum to be caused by the dipole moment components μ_x and μ_y, where the z axis is the C_3 axis in the high-symmetry nuclear configuration giving rise to the Jahn-Teller effect. For the nondegenerate electronic ground state of the $\boldsymbol{D}_{3h}(\text{M})$ molecule H_3^+ we showed above that pure rotational transitions in the vibrational ground state can arise because of intensity stealing from the ν_2 fundamental. Such pure rotational transitions will be extremely weak. In a degenerate electronic state, however, a $\boldsymbol{D}_{3h}(\text{M})$ molecule will have a pure rotational spectrum comparable in intensity with that of a normal polar molecule. That is, in the words of Scharf and Miller (1986), the molecule possesses an ***anomalous permanent dipole moment***. Watson (1986) points out that the rotational transitions in Jahn-Teller states should not be regarded as forbidden transitions analogous to those in nondegenerate electronic states. It arises from the third and fourth terms in Eq. (14-64) and is to be interpreted as the rotational structure of a so-called zero-frequency electronic transition.

Another interesting effect of the Jahn-Teller interaction is the occurrence of 'Jahn-Teller enhanced' fundamental bands. These are fundamental bands that steal intensity from the zero-frequency electronic transition. Watson (1986) has summarized the the symmetry conditions under which such enhanced bands can occur:

(A) The electronic state in question must generate electronic matrix elements $\mu_\alpha(e_i, e_i)$, $\mu_\alpha(e_j, e_j)$, $\mu_\alpha(e_i, e_j)$, ... with a degenerate MS group symmetry. The corresponding symmetry condition can be expressed as

$$\Gamma(\boldsymbol{T}) \otimes \left\{[\Gamma_{\mathrm{elec}}]^2 - \Gamma^{(s)}\right\} \supset \Gamma^{(s)}. \tag{14-67}$$

(B) The normal mode ν_r must be Jahn-Teller active [see Eq. (13-187)], i.e., the MS group symmetry Γ_r of the normal coordinate Q_r must satisfy

$$[\Gamma_{\mathrm{elec}}]^2 - \Gamma^{(s)} \supset \Gamma_r. \tag{14-68}$$

(C) The MS group symmetry Γ_r of the normal coordinate Q_r must also satisfy

$$\Gamma(\boldsymbol{T}) \otimes \{\Gamma_{\mathrm{elec}}\}^2 \supset \Gamma_r, \tag{14-69}$$

where $\{\Gamma_{\mathrm{elec}}\}^2$ indicates the antisymmetric product representation [see Eq. (6-120)].

Watson (1986) applies these conditions to various types of symmetric top and spherical top molecules, and gives a detailed discussion of the results.

14.1.12 Vibrational transitions

When $\Phi_{\mathrm{elec}}^{(e',S',m_S')} = \Phi_{\mathrm{elec}}^{(e'',S'',m_S'')}$ we can simplify Eq. (14-37) to

$$\Gamma''_{\mathrm{vib}} \otimes \Gamma'_{\mathrm{vib}} \supset \Gamma(\mu_\alpha) = \Gamma(T_\alpha). \tag{14-70}$$

A ***vibrationally allowed*** transition fulfills this condition for $\alpha = x$, y, or z. For a vibrational transition $\Phi'_{\mathrm{vib}} \neq \Phi''_{\mathrm{vib}}$ so that Eq. (14-41) becomes an expansion of the nuclear dipole moment in terms of its value at equilibrium and its dependence on the nuclear coordinates. Even when the equilibrium dipole moment is nonvanishing, i.e., $\mu_\alpha^{(0)}(e'',e'') \equiv \mu_\alpha^{(0)} \neq 0$, it will not contribute to the vibronic matrix elements of Eq. (14-26) because the vibrational wavefunctions of a single electronic state are orthogonal to each other. The most important contribution to the vibrational matrix elements is thus expected to originate in the terms of Eq. (14-41) linear in the normal coordinates Q_r. For this contribution to be nonvanishing we must have

$$\langle\Phi'_{\mathrm{vib}}|Q_r|\Phi''_{\mathrm{vib}}\rangle \neq 0 \tag{14-71}$$

and [as discussed in connection with Eq. (14-41), where we now have the additional constraint $\Phi_{\mathrm{elec}}^{(e',S',m_S')} = \Phi_{\mathrm{elec}}^{(e'',S'',m_S'')}$]

$$\Gamma(Q_r) = \Gamma(\mu_\alpha) = \Gamma(T_\alpha). \tag{14-72}$$

For Eq. (14-71) to be true in the harmonic oscillator approximation we have the selection rule

$$\Delta v_r = \pm 1, \tag{14-73}$$

where, from Eq. (14-72), the only allowed vibrational transitions are those for which the normal coordinate transforms like a translation. For vibrational transitions from the vibrational ground state only those $v_r = 1$ states are accessible (giving rise to *fundamental bands* in the spectrum) whose normal coordinates transform like a translation. Since the number of normal coordinates that transform like a translation differs if we make different assumptions about the equilibrium symmetry of the molecule, we can use the observed number of allowed fundamental bands to help us determine the equilibrium symmetry. Electrical and mechanical anharmonicity will give rise to forbidden transitions that do not satisfy Eq. (14-73), but Eq. (14-70) is still required. Rotation-vibration and rovibronic interactions will make additional forbidden transitions allowed [see Eq. (14-99)].

14.1.13 Rotational transitions

Rotational transitions will accompany the vibrational and vibronic transitions just discussed. In the approximation of a completely separable wavefunction, the selection rules on the rotational quantum numbers are derived from the product of the vibronic matrix element and the $3j$-symbol in Eq. (14-33), so that the selection rule on N is given by Eq. (14-34): $\Delta N = 0, \pm 1$.

For a symmetric top molecule K ($= |k|$) will normally be a useful near quantum number. It follows from the discussion given in connection with Eq. (14-40) that when K can be used to label the molecular states, and Eq. (14-40) is satisfied for a given value of α, then from the $\sigma' = k' - k$ requirement for the $3j$ symbol in Eq. (14-33) to be nonvanishing we obtain

$$\Delta K = 0 \quad \text{if} \quad \alpha = z \quad (\sigma' = 0) \tag{14-74}$$

and

$$\Delta K = \pm 1 \quad \text{if} \quad \alpha = x \text{ or } y \quad (\sigma' = \pm 1), \tag{14-75}$$

with the restriction that $\Delta N = 0$ is forbidden for $K = 0 \leftarrow 0$ [see Eq. (13-167) and Table 12-15].

Rotation-vibration interactions caused by centrifugal distortion and Coriolis coupling spoil K as a good quantum number for a symmetric top and hence give rise to forbidden transitions that do not satisfy Eqs. (14-74) and (14-75). However, the quantities g_{rv}, η and τ defined in Table 12-14 and in Eq. (12-78) are good quantum numbers and subject to useful selection rules. When we consider transitions within one electronic state, the respective symmetries Γ'_{rv} and Γ''_{rv} of the functions Φ'_{rv} and Φ''_{rv} [Eq. (13-217)] will satisfy

$$\Gamma'_{\mathrm{rv}} \otimes \Gamma''_{\mathrm{rv}} \supset \Gamma^{*}, \tag{14-76}$$

where Γ^{*} is the electric dipole representation. From Eq. (14-76) we obtain the selection rules on g_{rv}, η and τ given in Table 14-1.

Table 14-1

Selection rules for symmetric top transitions within one electronic state

Molecular symmetry group	Selection rules		
$C_{nv}(\mathrm{M})$ $(n \geq 3)$	$\Delta g_{rv} = 0$		$\Delta\tau$ odd
$D_{nh}(\mathrm{M})$ $(n \geq 3)$	$\Delta g_{rv} = 0$	$\Delta\eta$ odd	$\Delta\tau = 0$
$D_{nd}(\mathrm{M})$ $(n \geq 3$, n odd$)$	$\Delta g_{rv} = 0$	$\Delta\eta$ odd	$\Delta\tau = 0$
$D_{(n/2)d}(\mathrm{M})$ $(n/2 \geq 2$, $n/2$ even$)$	$\Delta g_{rv} = \frac{n}{2} + nt$		$\Delta\tau = 0$

The quantum numbers g_{rv} and η are defined in Table 12-14, and τ is defined in Eq. (12-78). We define $\Delta g_{rv} = g'_{rv} - g''_{rv}$, $\Delta\eta = \eta' - \eta''$, and $\Delta\tau = \tau' - \tau''$. t is an arbitrary integer.

If the rotational transitions within a vibrational or vibronic band of a symmetric top molecule satisfy Eq. (14-74) the band has a characteristic appearance and is called a *parallel band*, whereas Eq. (14-75) leads to a *perpendicular band*. As an example of a parallel band we consider the ν_3 band in the electronic ground state [of A_1 symmetry in $C_{3v}(\mathrm{M})$] of CH_3F shown in Fig. 14-5 [see Papoušek, Ogilvie, Civiš, and Winnewisser (1991)]. The ν_3 normal mode describes the C-F stretching motion. The dipole moment component μ_z of CH_3F has A_1 symmetry in $C_{3v}(\mathrm{M})$, μ_x and μ_y have E symmetry. The normal coordinate Q_3 has A_1 symmetry [Eq. (13-42)]. Consequently for the ν_3 band Eq. (14-40) is satisfied for $\alpha = z$, and Eq. (14-74) applies. In order to understand the structure of the band we use the expressions for the rotation-vibration energies of a prolate symmetric top given in Eqs. (13-127)-(13-133) (in which we must set $J = N$). We denote by G_0 and G_3 the values of G_{VL} calculated from Eq. (13-128) for the vibrational ground state and the ν_3 state of CH_3F, and we define $\tilde{\nu}_0 = G_3 - G_0$. Further, A_0 and B_0 are the A and B values for the vibrational ground state, A_3 and B_3 are the corresponding values for the ν_3 state, and we define $\Delta A_3 = A_3 - A_0$ and $\Delta B_3 = B_3 - B_0$. In Eq. (13-129) the dominant terms are those involving A_V, B_V, and $(A\zeta^z_{ta,tb})_V$; we neglect all other terms here. For both the vibrational ground state and the ν_3 state, the term involving $(A\zeta^z_{ta,tb})_V$ vanishes because in these two vibrational states, all $l_r = 0$. With these definitions and approximations we can write the wavenumber of a ν_3 band transition as

$$\begin{aligned}\tilde{\nu} = \tilde{\nu}_0 &+ (\Delta A_3 - \Delta B_3)\,(K'')^2 + \Delta B_3\,(N'' + \Delta N)\,(N'' + \Delta N + 1)\\ &+ B_0\,\Delta N\,(2N'' + \Delta N + 1).\end{aligned} \tag{14-77}$$

The N-value in the initial state (the vibrational ground state) is N'', and that in the final state (the ν_3 state) is $N' = N'' + \Delta N$, where the allowed values for ΔN are 0, ±1. Both the initial and the final states have the K-value K'' [Eq. (14-74)]. The absolute values of the parameters ΔA_3 and ΔB_3 in

Eq. (14-77) are small in comparison to B_0, so for moderate values of N'' and K'', the term involving B_0 will dominate. If we neglect the terms involving ΔA_3 and ΔB_3, Eq. (14-77) predicts that P branch lines ($\Delta N = -1$) are found at the wavenumbers $\tilde{\nu}_0 - 2B_0$, $\tilde{\nu}_0 - 4B_0$, $\tilde{\nu}_0 - 6B_0$, ..., all Q branch lines ($\Delta N = 0$) are found at the wavenumber $\tilde{\nu}_0$, and the R branch lines ($\Delta N = +1$) are found at the wavenumbers $\tilde{\nu}_0 + 2B_0$, $\tilde{\nu}_0 + 4B_0$, $\tilde{\nu}_0 + 6B_0$, ... Owing to the term involving $(K'')^2$ in Eq. (14-77) [and to some of the terms we have neglected in Eq. (13-129)] the transition wavenumbers will depend weakly on K''. Hence the P and R branch transitions having the same value of N'' but different values of K'' will cluster close to the positions given above, and the Q branch transitions will cluster close to the wavenumber $\tilde{\nu}_0$. Also the N''-dependent terms neglected here will cause small deviations from these predictions. However, a parallel band of a prolate symmetric top will have P and R branches consisting of nearly equidistantly spaced K *structure* , each such structure consisting of lines with a common N''-value but different K''-values, together with a Q branch whose transitions cluster tightly around the wavenumber $\tilde{\nu}_0$. The P branch lines are located at wavenumbers lower than $\tilde{\nu}_0$ and the R branch lines at higher wavenumbers. The structure described here is clearly recognized in Fig. 14-5.

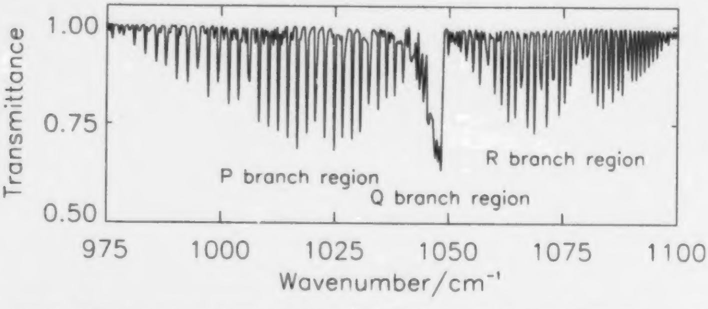

Fig. 14-5. The ν_3 band of CH_3F [Papoušek, Ogilvie, Civiš, and Winnewisser (1991)]. For this parallel band, $\tilde{\nu}_0 = 1048.6$ cm^{-1} (see text). The P, Q and R branch regions are indicated. In the P and R branch regions, there are regular series of K *structures* (see text). The spectrum also contains lines from the strong $2\nu_3 - \nu_3$ and $\nu_3 + \nu_6 - \nu_6$ hot bands.

The ν_6 band in the electronic ground state of CH_3F [Papoušek, Tesař, Pracna, Civiš, Winnewisser, Belov, and Tretyakov (1991)] is an example of a perpendicular band (Fig. 14-6). The normal coordinates (Q_{6a}, Q_{6b}) describe the CH_3 rocking mode. They have E symmetry in $C_{3v}(M)$ [Eq. (13-42)] so that for the ν_6 band Eq. (14-40) is fulfilled for $\alpha = x$ and y, and Eq. (14-75) applies. In the upper vibrational state (the ν_6 state) of this band $l_6 = \pm 1$ and $l_4 = l_5 = 0$, and in the lower vibrational state (the vibrational ground state) all $l_r = 0$. From the selection rule $\Delta g_{rv} = 0$ in Table 14-1, together with Eq. (14-75) and the definition of g_{rv} for a C_{3v} molecule in Table 12-14, we find that for an allowed rotation-vibration transition in the ν_6 band the l_6 value in the upper vibrational state enters into the selection rules as

$$l_6 = K' - K'' = \Delta K = \pm 1, \tag{14-78}$$

where, as usual, K'' is the K-value in the initial state of the transition and K' the value in the final state.

Equations (13-128) and (13-130)-(13-133) show that the two ν_6 states with $l_6 = \pm 1$ have common values of G_{VL} and $(A\zeta^z_{ta,tb})_V$ respectively, and we denote these values by G_6 and $(A\zeta^z_{6a,6b})_6$. It is left as an exercise for the reader to show, by using Eq. (14-78) together with Eqs. (13-127)-(13-129), that in the ν_6 perpendicular band the transition wavenumbers are given approximately by

$$\tilde{\nu} = \tilde{\nu}_{K,\Delta K} + B_0\,\Delta N\,(2N'' + \Delta N + 1)\,, \tag{14-79}$$

(where $\tilde{\nu}_{K,\Delta K}$ is defined below) so that the P branch lines ($\Delta N = -1$) are found at the wavenumbers $\tilde{\nu}_{K,\Delta K} - 2B_0$, $\tilde{\nu}_{K,\Delta K} - 4B_0$, $\tilde{\nu}_{K,\Delta K} - 6B_0$, ..., all Q branch lines ($\Delta N = 0$) are found at the wavenumber $\tilde{\nu}_{K,\Delta K}$, and the R branch lines ($\Delta N = +1$) are found at the wavenumbers $\tilde{\nu}_{K,\Delta K} + 2B_0$, $\tilde{\nu}_{K,\Delta K} + 4B_0$, $\tilde{\nu}_{K,\Delta K} + 6B_0$, ... We say that the P, Q and R branches with common values of K and ΔK, whose individual transitions have $N'' = K''$, $K'' + 1$, $K'' + 2$, ..., form a ***subband***. In a first approximation, the ***subband origin*** is given by

$$\tilde{\nu}_{K,\Delta K} = \tilde{\nu}_0 + 2\left[A_0 - B_0 - \left(A\zeta^z_{6a,6b}\right)_6\right]\Delta K\,K'' + (A_0 - B_0)\,\Delta K^2, \tag{14-80}$$

where $\tilde{\nu}_0 = G_6 - G_0$, $\Delta K = \pm 1$ and $K'' = 0, 1, 2, \ldots$. In a parallel band there are also subbands, but they all have subband origins close to $\tilde{\nu}_0$ so that they very nearly coincide. In the perpendicular band the subbands have near-equidistantly spaced subband origins, the distance between two neighboring origins being approximately $2[A_0 - B_0 - (A\zeta^z_{6a,6b})_6]$. Consequently, in a perpendicular band of a symmetric top molecule the individual rotation-vibration transitions are more spread out than in a parallel band, and the perpendicular band makes a less ordered impression as seen in Fig. 14-6. Normally, the dominating features in a perpendicular band is the series of Q branches with $\Delta K\,K'' = \ldots, -4, -3, -2, -1, 0, 1, 2, 3, 4, \ldots$. A number of such Q branches can be recognized in Fig. 14-6, they are marked by their respective values of $\Delta K\,K''$. The Q branches with $\Delta K\,K'' = -3$, 0, 3 and 6 are clearly stronger than the neighboring Q branches; this is because of the spin statistical weight factors[8] of CH_3F discussed in Section 13.6.3. An unusual feature in the ν_6 band of CH_3F is the fortuitous clustering of P branch lines between 1120 and 1160 cm^{-1}. It can be seen from the line lists of Papoušek, Tesař, Pracna, Civiš, Winnewisser, Belov, and Tretyakov (1991) that in this region seemingly unrelated P branch lines cluster together forming the regular structure in Fig. 14-6.

The difference in structure between parallel bands and perpendicular bands provides a useful diagnostic for the vibrational or vibronic states involved in

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[8] For the $K = 0$ Q-branch the intensity is enhanced because of the square of $1/\sqrt{2}$ that does not occur when one calculates intensities involving $K = 0$ wavefunctions.

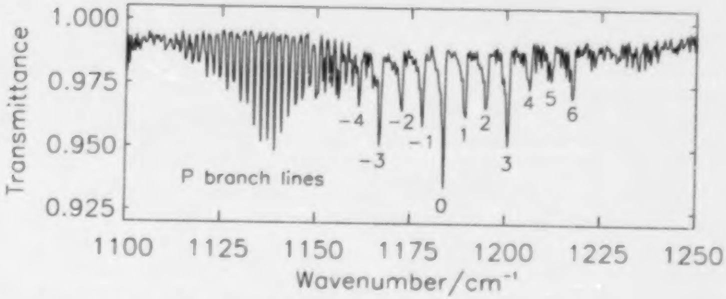

Fig. 14-6. The ν_8 band of CH_3F [Papoušek, Tesař, Pracna, Civiš, Winnewisser, Belov, and Tretyakov (1991)]. For this perpendicular band, $\tilde{\nu}_0 = 1182.7$ cm^{-1} (see text). The Q branches are marked by their values of $\Delta K\, K''$.

a given transition, since it tells us the symmetry relationship between them [from Eq. (14-55)]. If the transition involves a degenerate vibronic state then selection rules on the ($\pm l$) label (see page 339) can be derived from the results in Table 14-1 and these are useful [see Hougen (1962c), Mills (1964a) and Herzberg (1991b), page 224]. In particular, transitions from an A vibronic state to an E or E_1 vibronic state (in which the vibronic symmetry species are connected by the species of T_x and T_y) are such that the $\Delta K = +1$ transitions are to the ($+l$) levels and $\Delta K = -1$ transitions are to the ($-l$) levels. For the example considered here, this selection rule follows from Eq. (14-78).

For an asymmetric top molecule we can derive general selection rules on the $K_a K_c$ quantum numbers by means of the rotation group $\boldsymbol{D}_2$. To do this we rewrite Eq. (14-12) as

$$\mu_A = \lambda_{aA}\mu_a + \lambda_{bA}\mu_b + \lambda_{cA}\mu_c, \qquad (14\text{-}81)$$

where $A = \xi,\ \eta,\ \zeta$ labels the space fixed axes, and the molecule fixed axes are denoted a, b, c according to the convention discussed in connection with Eqs. (11-8) and (11-9). For an asymmetric top molecule, we can write the separable wavefunction $\Phi_{\rm int}$ as $\Phi_{\rm nspin}\,|N_{K_a K_c}\rangle\,\Phi_{\rm vib}\Phi_{\rm elec}^{(e,S,m_S)}$, where $|N_{K_a K_c}\rangle$ is an eigenfunction of the rigid asymmetric rotor. In order to calculate the line strength from Eq. (14-5) we need the matrix element

$$\langle\Phi'_{\rm int}\,|\mu_A|\,\Phi''_{\rm int}\rangle = \langle\Phi'_{\rm nspin}|\Phi''_{\rm nspin}\rangle \sum_{\alpha=a,b,c} \langle\Phi'_{\rm vib}\,|\mu_\alpha(e',e'')|\,\Phi''_{\rm vib}\rangle$$
$$\times\left\langle N'_{K'_a K'_c}\,|\lambda_{\alpha A}|\,N''_{K''_a K''_c}\right\rangle, \qquad (14\text{-}82)$$

where we have used Eq. (14-38). From the analytical form of the $\lambda_{\alpha A}$ functions [see Eq. (10-7)] it is easy to show that $\lambda_{\alpha A}$ has B_α symmetry ($\alpha = a$, b, or c; see Table 12-16) in the rotation group $\boldsymbol{D}_2$. If we apply the vanishing integral rule (using the irreducible representations of the group $\boldsymbol{D}_2$) to the rotational matrix element $\left\langle N'_{K'_a K'_c} \left| \lambda_{\alpha A} \right| N''_{K''_a K''_c} \right\rangle$ in Eq. (14-82) we derive from the results of Table 12-16 the following general selection rules on $K_a K_c$:

$$\begin{aligned} &\Delta K_a = \text{even} &&\Delta K_c = \text{odd} &&\text{if } \alpha = a, \\ &\Delta K_a = \text{odd} &&\Delta K_c = \text{odd} &&\text{if } \alpha = b, \\ &\Delta K_a = \text{odd} &&\Delta K_c = \text{even} &&\text{if } \alpha = c, \end{aligned} \tag{14-83}$$

all with $\Delta N = 0, \pm 1$ in the case of separable wavefunctions. A rotation-vibration band for which only $\langle \Phi'_{\text{vib}} | \mu_a(e', e'') | \Phi''_{\text{vib}} \rangle$, say, is nonvanishing, so that the selection rules on $K_a K_c$ are as given in Eq. (14-83) for $\alpha = a$, is said to be a *Type a band* (and to contain *Type a transitions*). *Type b (or c) bands* and transitions are defined analogously. If more than one of the three vibronic matrix elements $\langle \Phi'_{\text{vib}} | \mu_\alpha(e', e'') | \Phi''_{\text{vib}} \rangle$ are nonvanishing we speak about a *hybrid band*. If, for the states concerned, the molecule is a near prolate rotor (i.e., K_a is a useful near quantum number) then ΔK_a = even (or odd) can be replaced by $\Delta K_a = 0$ (or ± 1); for a near oblate rotor similar remarks apply to ΔK_c. Transitions obeying Eq. (14-83) but not obeying these more restrictive selection rules on ΔK_a or ΔK_c, as appropriate, can also be called forbidden. For spherical top molecules we just have $\Delta N = 0, \pm 1$ as the rotational selection rule when the wavefunction is separable.

Pure rotational transitions (in which the vibronic state does not change, i.e., $\Phi'_{\text{vib}} = \Phi''_{\text{vib}}$ and $\Phi_{\text{elec}}^{(e', S', m'_S)} = \Phi_{\text{elec}}^{(e'', S'', m''_S)}$) can occur with the rotational selection rules given above if the vibronic state is such that [for Eq. (14-26) to be nonvanishing]

$$\Gamma_{\text{ve}} \otimes \Gamma_{\text{ve}} \supset \Gamma(\mu_\alpha) = \Gamma(T_\alpha). \tag{14-84}$$

For a nondegenerate vibronic state Eq. (14-84) is satisfied only if $\Gamma(T_\alpha)$ is the totally symmetric representation of the MS group. If Eq. (14-84) is satisfied the molecule can have a nonvanishing *permanent dipole moment* given by

$$\langle \Phi_{\text{vib}} | \mu_\alpha(e, e) | \Phi_{\text{vib}} \rangle = \mu_\alpha^{(0)}, \tag{14-85}$$

where $\alpha = x, y$, or z. Note that the diagonal matrix element of $\mu_s^{(1,\sigma)}$ in the complete wavefunction Φ_{int} must vanish for a nondegenerate Φ_{int} state since $\mu_s^{(1,\sigma)}$ only has nonvanishing matrix elements between states of opposite parity. In a symmetric top molecule of $\boldsymbol{C}_{n\text{v}}$ symmetry the translational coordinate T_z is totally symmetric so that such molecules can have a nonvanishing permanent dipole moment in the z direction. In these circumstances pure rotational transitions are allowed with selection rules $\Delta K = 0, \Delta N = 0, \pm 1$ in the case of separable wavefunctions. For an asymmetric top the selection rules on K_a and K_c depend on the direction of the permanent dipole moment [i.e., on the values of α in Eq. (14-84)]. If the direction of the permanent dipole moment is along an axis that is not a principal inertial axis then allowed hybrid transitions occur with selection rules given by two, or all three, of Eq. (14-83) depending on the projection of that axis direction on the a, b and c axes. If none of the T_α are totally symmetric in the MS group, for a given molecule, then nondegenerate vibronic states cannot have a permanent dipole moment and pure rotational transitions are forbidden within such vibronic states.

14.1.14 An example: The forbidden rotational spectrum of H_3^+

The molecular ion H_3^+ has an equilateral triangular equilibrium structure, and its MS group is $\boldsymbol{D}_{3h}(M)$ (Table A-10). In Fig. 14-7 we show an H_3^+ molecule at equilibrium together with the xyz molecule fixed axis system. The x and y axes are in the plane defined by the three nuclei, and the z axis is perpendicular to this plane so that the (x, y, z) axes form a right-handed axis system. We consider here rotation-vibration transitions of H_3^+ within the ${}^1A_1{}'$ electronic ground state. The translational coordinates T_x and T_y transform together as species E' of $\boldsymbol{D}_{3h}(M)$, and the translational coordinate T_z transforms as $A_2{}''$. Since none of the T_α transform as the totally symmetric species $A_1{}'$ the molecule has no permanent dipole moment and the pure rotational spectrum is forbidden. However, rotation-vibration interaction can give intensity to such forbidden rotational transitions in this nonpolar molecule.

Before introducing the effect of the rotation-vibration interaction let us try to calculate the line strength of a rotational transition in H_3^+ from Eq. (14-33). The H_3^+ ion has two normal vibrational modes, ν_1 of $A_1{}'$ symmetry and ν_2 of E' symmetry in $\boldsymbol{D}_{3h}(M)$. We denote the separable rotation-vibration wavefunctions of H_3^+ as $|v_1, v_2, l_2; N, k, m\rangle$, and the vibrational wavefunctions as $|v_1, v_2, l_2\rangle$. Rotational transitions within the vibronic ground state of H_3^+, i.e., transitions $|v_1, v_2, l_2; N, k, m\rangle = |0, 0, 0; N', k', m'\rangle \leftarrow |0, 0, 0; N'', k'', m''\rangle$, satisfy $\Delta N = N' - N'' = 0, \pm 1$ [Eq. (14-34)], and it is further seen from Tables 12-14 (page 294) and 14-1 (page 444) that they must satisfy the selection rules $\Delta k = k' - k'' = \pm 3, \pm 9, \pm 15, \ldots$. However, if we try to calculate the line strength for such rotational transitions in the approximation of a completely separable wavefunction [i.e., from Eq. (14-33)], we discover that the line strength vanishes because it is dependent on the two vibronic integrals $\langle 0, 0, 0\,|\mu_x(e'', e'')|\,0, 0, 0\rangle$ and $\langle 0, 0, 0\,|\mu_y(e'', e'')|\,0, 0, 0\rangle$, which are the diagonal matrix elements of the electronic integrals $\mu_x(e'', e'')$ and $\mu_y(e'', e'')$ [components of the ground state dipole moment function, see Eq. (14-38)] with the vibrational function $|v_1, v_2, l_2\rangle = |0, 0, 0\rangle$. These two matrix elements vanish because they do not satisfy Eq. (14-40): the vibrational function $|0, 0, 0\rangle$ has $A_1{}'$ symmetry so we have $\Gamma''_{\text{vib}} = \Gamma'_{\text{vib}} = A_1{}'$ and thus $\Gamma''_{\text{vib}} \otimes \Gamma'_{\text{vib}} = A_1{}'$, but $\Gamma\left(\mu_x(e'', e''), \mu_y(e'', e'')\right) = E'$.

For H_3^+ the vibronic matrix elements $\langle 0, 0, 0\,|\mu_\alpha(e'', e'')|\,0, 1, \pm 1\rangle$, $\alpha = x$ or y, satisfy Eq. (14-40) since the functions $|v_1, v_2, l_2\rangle = |0, 1, \pm 1\rangle$ transform according to the E' irreducible representation of $\boldsymbol{D}_{3h}(M)$. Hence, rotation-vibration transitions in the ν_2 fundamental band are allowed in the approximation of a completely separable wavefunction. It follows from Tables 12-14 and 14-1 that

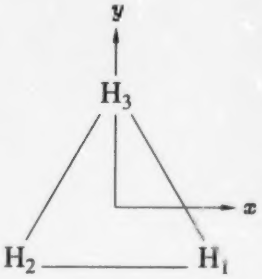

Fig. 14-7. The equilibrium structure and the definition of the molecule fixed axis system for an H_3^+ molecule.

the two types of transitions in the ν_2 band,

$$|0,1,1;N',k''+1,m''\rangle \leftarrow |0,0,0;N'',k'',m''\rangle \tag{14-86}$$

and

$$|0,1,-1;N',k''+2,m''\rangle \leftarrow |0,0,0;N'',k''+3,m''\rangle \tag{14-87}$$

are allowed if $\Delta N = 0, \pm 1$. From Table 12-14 we see that each of the two completely separable wavefunctions

$$|0,1,-1;N'',k''+2,m''\rangle \;\text{ and }\; |0,0,0;N'',k'',m''\rangle$$

belong to the same irreducible representation in $\boldsymbol{D}_{3h}(\mathrm{M})$, and so do

$$|0,1,1;N',k''+1,m''\rangle \;\text{ and }\; |0,0,0;N',k''+3,m''\rangle\,.$$

Thus, when we diagonalize a matrix representation of the rotation-vibration Hamiltonian in the basis set $|v_1, v_2, l_2; N, k, m\rangle$ as indicated by Eq. (13-217), in order include rotation-vibration interaction, each of these two basis function pairs will be mixed. Detailed examination shows that for H_3^+ the mixing is caused by the centrifugal distortion terms given in Eq. (13-6).

The interaction is very weak since the difference between the zero order energies is approximately equal to the vibrational energy of the ν_2 state, and so we can expect that the rotation-vibration problem will have a solution with the following dominant contributions

$$\begin{aligned}|\Phi''_{\mathrm{rv}}\rangle &= c''_0\,|0,0,0;N'',k'',m''\rangle \\ &\quad + c''_2\,|0,1,-1;N'',k''+2,m''\rangle + \ldots\,,\end{aligned} \tag{14-88}$$

where $|c''_0| \approx 1$ and $|c''_2| \ll 1$. Similarly, there will be another solution essentially given by

$$\begin{aligned}|\Phi'_{\mathrm{rv}}\rangle &= c'_0\,|0,0,0;N',k''+3,m''\rangle \\ &\quad + c'_2\,|0,1,1;N',k''+1,m''\rangle + \ldots\,.\end{aligned} \tag{14-89}$$

where $|c_0'| \approx 1$ and $|c_2'| \ll 1$. Both of the rotation-vibration wavefunctions $|\Phi_{\rm rv}''\rangle$ and $|\Phi_{\rm rv}'\rangle$ can obviously be labeled as belonging to the vibrational ground state, since the basis functions with the dominant contribution to the wavefunctions have $v_1 = v_2 = 0$. The point is, however, that when we take into account rotation-vibration interaction we obtain contributions to the wavefunctions from basis functions belonging to other vibrational states, such as the ν_2 state considered here. This has the consequence that when we calculate the line strength for the transition $|\Phi_{\rm rv}'\rangle \leftarrow |\Phi_{\rm rv}''\rangle$ (we have already checked above that this transition satisfies the selection rules given in Table 14-1) with the wavefunctions of Eqs. (14-88) and (14-89), we determine the rotation-vibration matrix element $\left\langle \Phi_{\rm rv}' \left| \mu_{\rm s}^{(1,\sigma)} \right| \Phi_{\rm rv}'' \right\rangle$ entering into the line strength of Eq. (14-17) to have the following dominant contributions

$$\begin{aligned}
&\left\langle \Phi_{\rm rv}' \left| \mu_{\rm s}^{(1,\sigma)} \right| \Phi_{\rm rv}'' \right\rangle \\
&= (c_0')^* c_2'' \left\langle 0,0,0; N', k''+3, m'' \left| \mu_{\rm s}^{(1,\sigma)} \right| 0,1,-1; N'', k''+2, m'' \right\rangle \\
&+ (c_2')^* c_0'' \left\langle 0,1,1; N', k''+1, m'' \left| \mu_{\rm s}^{(1,\sigma)} \right| 0,0,0; N'', k'', m'' \right\rangle + \ldots . \qquad (14\text{-}90)
\end{aligned}$$

The two matrix elements on the right hand side of Eq. (14-90) are nonvanishing because they determine the intensities of the allowed transitions given in Eq. (14-86) and (14-87).

We describe the transition $|\Phi_{\rm rv}'\rangle \leftarrow |\Phi_{\rm rv}''\rangle$ discussed here as a rotational transition with $k = k'' + 3 \leftarrow k''$ in the vibronic ground state of H_3^+. In Fig. 14-8, we show schematically the interactions giving rise to the intensity stealing that gives this transition a nonvanishing intensity. We see that if we attempt to calculate the line strength of such a transition in the approximation of a completely separable wavefunction the line strength vanishes. However, if we use the less approximate rotation-vibration wavefunctions of Eqs. (14-88) and (14-89) the line strength acquires a nonvanishing contribution given by Eq. (14-90) for $N' - N'' = 0, \pm 1$. The resulting intensity will be very small because $|c_2''| \ll 1$ and $|c_2'| \ll 1$. The rotational spectrum in the vibronic ground state of H_3^+ thus consists of forbidden transitions obeying the selection rule $k' - k'' = \pm 3$ (in the above example, we consider a transition with $k' - k'' = 3$, but by interchanging the k values in the initial and final states we can easily produce one with $k' - k''$ $= -3$), whose intensities are induced by rotation-vibration interaction. This is an example of intensity stealing caused by rotation-vibration interaction. The pure rotational spectrum of H_3^+ steals intensity from the ν_2 fundamental band. So far, these transitions have not been observed.

As a further example of intensity stealing caused by rotation-vibration interaction, we show in Fig. 14-9a the ν_1 band of diazirine $H_2{}^{12}C^{14}N_2$ and in Fig. 14-9b the corresponding spectral region for $H_2{}^{12}C^{15}N_2$ [Winnewisser, Gambi, and Winnewisser (1994)]. In $H_2{}^{12}C^{15}N_2$, anharmonic resonances (see page 329) between the ν_1 state and the $\nu_2 + \nu_3$ and $2\nu_7 + \nu_3$ states cause three bands of nearly equal intensity. This type of intensity stealing occurs frequently in high-vibrational overtone spectroscopy. An interesting example

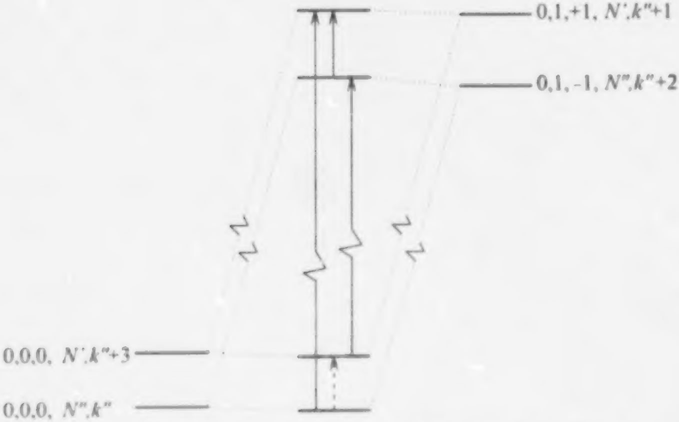

Fig. 14-8. Schematic interaction diagram for an H_3^+ molecule showing the mechanism leading to nonvanishing intensities for rotational transitions in the vibrational ground state. The basis states shown in the left and right hand columns are labeled by v_1, v_2, l_2, N, k. These basis states interact as indicated by the dotted lines to produce the molecular eigenstates shown in the middle column. Solid arrows indicate transitions between the eigenstates whose line strengths are nonvanishing when calculated in the approximation of a completely separable wavefunction. The forbidden rotational transition in the vibrational ground state, which steals intensity from the two ν_2 transitions, is shown as a dashed arrow.

is given for methanol CH_3OH by Lubich, Boyarkin, Settle, Perry, and Rizzo (1995) [see also the comment on this work by Mills (1995)].

Watson (1971b) has shown that rotation-vibration interaction caused by centrifugal distortion can produce a dipole moment, and hence a pure rotation spectrum, in the ground vibronic state of any nonpolar molecule belonging to one of several point groups without a center of symmetry, including $\boldsymbol{D}_{3h}$, $\boldsymbol{D}_n$, $\boldsymbol{D}_{2d}$ and $\boldsymbol{T}_d$ [see also Dorney and Watson (1972)]. The forbidden rotational spectrum of methane CH_4 is an an important example for which the forbidden transitions have been observed. The forbidden transitions satisfy Eq. (14-76) [see, for example, Hougen (1976)].

We have used H_3^+ as an example of rotation-vibration intensity stealing because it has only one fundamental transition from which the rotational transitions can steal intensity. In a larger molecule there could be several vibrational modes of the appropriate symmetry, and the rotational transitions would steal intensity from all the corresponding fundamental transitions. It should be noted, however, that because H_3^+ is very light, its vibrational amplitudes are so large that the rotation-vibration motion is poorly described by the harmonic oscillator-rigid rotor model employed here. Accurate calculations of the rotation-vibration energies and intensities for H_3^+ require more sophisticated models (see Section 13.2.5). Such models have been used by Jensen and Špirko (1986) and by Miller, Tennyson, and Sutcliffe (1990) to calculate the intensities of the forbidden rotational transitions discussed above. The two calculations

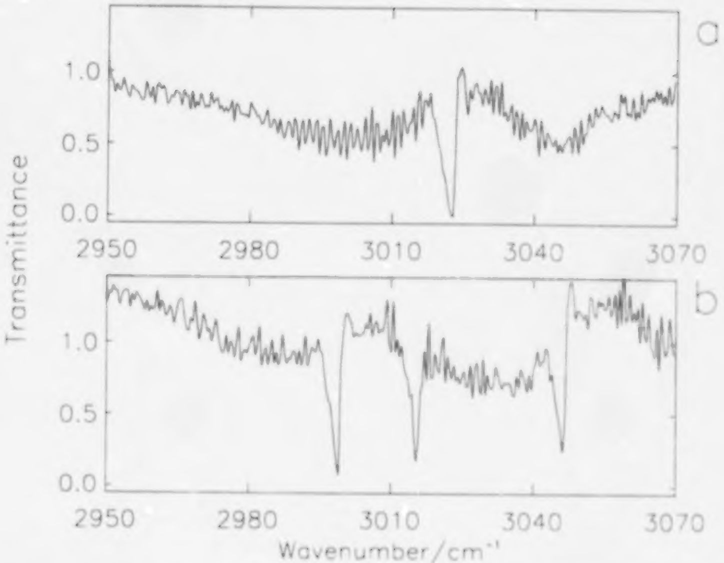

Fig. 14-9. a: The ν_1 band of diazirine $H_2{}^{12}C^{14}N_2$ and b: the corresponding spectral region for $H_2{}^{12}C^{15}N_2$ [Winnewisser, Gambi, and Winnewisser (1994)].

produce similar results.

14.1.15 The effective dipole moment operator

We review the calculation of rotation and rotation-vibration intensities using the contact transformation technique described in Section 13.2.4. For more details we refer the reader to the review article by Aliev and Watson (1985), who base their calculation of the line strength on Eq. (14-5) (i.e., they do not transform to irreducible spherical tensor operators as we do here). The intensities of rotation-vibration transitions within one electronic state $\Phi_{\mathrm{elec}}^{(e,S,m_S)}$ are determined by the matrix elements

$$\left\langle \Phi'_{\mathrm{rv}} \Phi_{\mathrm{elec}}^{(e,S,m_S)} \left| \mu_A \right| \Phi_{\mathrm{elec}}^{(e,S,m_S)} \Phi''_{\mathrm{rv}} \right\rangle = \left\langle \Phi'_{\mathrm{rv}} \left| \mu_A(e,e) \right| \Phi''_{\mathrm{rv}} \right\rangle , \tag{14-91}$$

where the wavefunctions Φ'_{rv} and Φ''_{rv} are given by Eq. (13-217), and

$$\mu_A(e,e) = \left\langle \Phi_{\mathrm{elec}}^{(e,S,m_S)} \left| \mu_A \right| \Phi_{\mathrm{elec}}^{(e,S,m_S)} \right\rangle = \sum_{\alpha=x,y,z} \lambda_{\alpha A} \mu_\alpha(e,e). \tag{14-92}$$

Here we use Eq. (14-12) to express the space fixed dipole moment component μ_A in terms of the molecule fixed components $\mu_\alpha(e,e)$ defined in Eq. (14-38).

Using Eq. (13-120) to express the rotation-vibration wavefunctions $\Phi'_{\rm rv}$ and $\Phi''_{\rm rv}$ we obtain

$$\begin{aligned}\langle\Phi'_{\rm rv}\,|\mu_A(\epsilon,e)|\,\Phi''_{\rm rv}\rangle &= \left\langle e^{-i\hat{S}}\Phi_{\rm rv}^{(V',L',N',k',m')}\,|\mu_A(\epsilon,e)|\,e^{-i\hat{S}}\Phi_{\rm rv}^{(V'',L'',N'',k'',m'')}\right\rangle\\ &= \left\langle \Phi_{\rm rv}^{(V',L',N',k',m')}\left|e^{i\hat{S}}\mu_A(\epsilon,e)e^{-i\hat{S}}\right|\Phi_{\rm rv}^{(V'',L'',N'',k'',m'')}\right\rangle .\end{aligned} \tag{14-93}$$

That is, we can formally calculate the matrix element in Eq. (14-91) as the matrix element between two completely separable basis functions $\Phi_{\rm rv}^{(V',L',N',k',m')}$ and $\Phi_{\rm rv}^{(V'',L'',N'',k'',m'')}$ of the *effective dipole moment operator*

$$\tilde{\mu}_A(\epsilon,e) = e^{i\hat{S}}\mu_A(\epsilon,e)e^{-i\hat{S}}, \tag{14-94}$$

which is obtained from the "untransformed" dipole moment operator $\mu_A(\epsilon,e)$ by exactly the same transformation that was applied to the rotation-vibration Hamiltonian in Eq. (13-110). The operator $\tilde{\mu}_A(\epsilon,e)$ is given by an expression analogous to Eqs. (13-115)-(13-117):

$$\tilde{\mu}_A(\epsilon,e) = \mu_A(\epsilon,e) + i\left[\hat{S},\mu_A(\epsilon,e)\right] - \frac{1}{2}\left[\hat{S},\left[\hat{S},\mu_A(\epsilon,e)\right]\right] + \ldots . \tag{14-95}$$

We do not discuss the derivation of $\tilde{\mu}_A(\epsilon,e)$ in detail. We only note that this operator is obtained as a sum of terms, each term being a constant coefficient multiplied by powers of the normal coordinates Q_r, their conjugate momenta P_r, the direction cosine matrix elements $\lambda_{\alpha A}$ and the angular momentum components $(\hat{N}_x, \hat{N}_y, \hat{N}_z)$. That is, we can expand $\tilde{\mu}_A(\epsilon,e)$ in a manner analogous to Eq. (13-121):

$$\tilde{\mu}_A(\epsilon,e) = \sum_{m=0}^{\infty}\sum_{n=1}^{\infty}\tilde{\mu}_A(\epsilon,e)_{mn} \tag{14-96}$$

where we can write the operator $\tilde{\mu}_A(\epsilon,e)_{mn}$ symbolically as

$$\tilde{\mu}_A(\epsilon,e)_{mn} = \left(Q_r, P_r\right)^m\left(\lambda_{\alpha A}, \hat{N}_\alpha\right)^n, \tag{14-97}$$

so that $\tilde{\mu}_A(\epsilon,e)_{mn}$ contains all terms of degree m in the vibrational operators [Q_r or P_r; $r = 1, 2, 3, \ldots$] and of degree n in the rotational operators [$\lambda_{\alpha A}$ or $\hat{N}_\alpha$; $\alpha = x, y$, or z, and $A = \xi, \eta, \zeta$].

In Eq. (14-90) we give the matrix elements determining the intensities of the forbidden rotational transitions in the vibrational ground state of H_3^+. In the effective dipole moment theory just outlined, these intensities are determined by the matrix elements between $\Phi_{\rm rv}^{(V,L,N',k',m')}$ and $\Phi_{\rm rv}^{(V,L,N'',k'',m'')}$ of the operator

$$\tilde{\mu}_A(\epsilon,e)_{03} = \frac{1}{2}\sum_{\alpha,\beta,\gamma=x,y,z}\Theta_\gamma^{\alpha\beta}\left(\hat{N}_\alpha\hat{N}_\beta\lambda_{\gamma A} + \lambda_{\gamma A}\hat{N}_\beta\hat{N}_\alpha\right). \tag{14-98}$$

where the coefficients $\Theta_\gamma^{\alpha\beta}$ are given by Eq. (136) of Aliev and Watson (1985). A detailed treatment of forbidden transitions in X_3 molecules, using the effective dipole moment operator formalism, is given by Aliev and Mikhailov (1984) [see also Pan and Oka (1986)].

14.1.16 Electric dipole transitions: Summary

The strongest vibronic transitions are expected to be those that are electronically allowed so that they satisfy Eqs. (14-52) and (14-53). The strongest vibrational transitions within one electronic state are expected to be the fundamental bands which satisfy Eqs. (14-72) and (14-73). For symmetric top molecules the strongest rotational lines accompanying these transitions will satisfy Eqs. (14-74) and (14-75) so that they have $|\Delta K| \leq 1$, and for an asymmetric top the rotational lines will satisfy Eq. (14-83) (with 'odd' = ±1 and 'even' = 0). The strongest pure rotational transitions will occur within vibronic states that satisfy Eq. (14-84) with rotational selection rules as given by Eqs. (14-74) and (14-75) for symmetric tops and Eq. (14-83) for asymmetric tops (with 'odd' = ±1 and 'even' = 0). All transitions that do not satisfy these selection rules are called forbidden transitions.

Vibronic interactions and the dependence of the electronic transition moment on the nuclear coordinates give rise to forbidden electronic transitions that do not satisfy Eq. (14-52) but which still satisfy Eq. (14-55). Mechanical and electrical anharmonicity give rise to vibrational transitions that do not satisfy Eqs. (14-71)-(14-73) but which satisfy Eq. (14-70), and rotation-vibration interaction and axis-switching spoil the selection rules of Eqs. (14-74), (14-75), and (14-83), although Eq. (14-76) must be satisfied [rotation-vibration interaction can also give rise to forbidden rotational transitions within a vibronic state for which Eq. (14-84) is not satisfied]. Rovibronic interaction and interaction involving the electron spin, such as electron spin–orbit coupling, relax the rovibronic selection rule to

$$\Gamma'_{\mathrm{rve}} \otimes \Gamma''_{\mathrm{rve}} \supset \Gamma^* \tag{14-99}$$

where $\Gamma_{\mathrm{rve}} = \Gamma_{\mathrm{elec}} \otimes \Gamma_{\mathrm{rv}}$. Finally nuclear spin interaction relaxes the selection rules completely to those of Eqs. (14-8) and (14-11) when ortho-para type transitions become allowed. Ortho-para transitions in methane have been observed by Ozier, Yi, Khosla, and Ramsey (1970) [see the Bibliographical Notes at the end of the chapter]. Forbidden transitions are particularly important in circumstances in which their occurrence allows otherwise inaccessible energy level separations in a molecule to be determined [as, for example, in the determination of A_0 from the infrared spectrum of a symmetric top molecule; Olson (1972), Sarka (1976)]. Except in the case of resonances (when the interaction spoiling the selection rules is between levels that are close lying in energy) forbidden transitions are much weaker than allowed transitions.

Centrosymmetric molecules merit special attention. For a centrosymmetric molecule the species of the translations T_α are always u since the operation[9] $\hat{O}_i$ inverts the vibronic coordinates in the molecule fixed axis system. Thus allowed vibrational or vibronic transitions must obey the selection rule u ↔ g. The rotational levels within a g (u) vibronic state are all of g (u) symmetry since the rotational wavefunctions must all be of g symmetry. The irreducible representation Γ^* spanned by each of the space fixed electric dipole moment components μ_A, where $A = \xi$, η or ζ, must be u ($\hat{O}_i$ is a permutation-inversion operation and must reverse μ_A), and consequently no rotational transitions within any vibronic state of a centrosymmetric molecule can occur as a result of rotation-vibration or rovibronic interactions. Electron spin functions in either a case (a) or case (b) basis must be of g species so that spin–orbit coupling cannot induce rotational transitions. Only interactions involving the nuclear spins can induce pure rotational transitions to occur in a centrosymmetric molecule. Such transitions will be ortho-para type transitions, and the presence of identical nuclei with nonzero spin is required. These forbidden transitions are most likely to be observed in one of a pair of close lying electronic states if one is of g symmetry and the other of u symmetry, when a magnetic interaction between the nuclear spins and the electrons (from $\hat{H}_{\mathrm{nso}} + \hat{H}_{\mathrm{nses}}$ in Table 7-1) mixes levels and spoils the g/u classification. In Section 17.7 we discuss electronic g/u mixing (or, equivalently, ortho-para mixing) in H_2^+ in more detail.

In molecules that are not centrosymmetric, but which do not have a permanent dipole moment, rotation-vibration or rovibronic interactions can give rise to an allowed rotational spectrum as long as Eq. (14-76) or (14-99) is obeyed. The forbidden rotational spectrum of CH_4 is caused by rotation-vibration interactions and Eq. (14-76) is satisfied by the observed transitions. The forbidden rotational spectrum of HD is caused by rovibronic interaction and Eq. (14-99) is satisfied by the observed transitions [see, for example, Bunker (1973)].

If we neglect electrical and mechanical anharmonicity only $\Delta v_r = 1$ transitions are allowed. However, with modern experimental techniques it is possible to detect transitions with high values of Δv_r; values of $\Delta v_r = 5$ and more are not uncommon. The study of such vibrational transitions, ***vibrational overtone spectroscopy***, is of great interest. The observed transitions mostly involve high excitation of H-stretch vibrations [i.e., the stretching of bonds between hydrogen atoms and other atoms in the molecule]. These vibrations have large amplitudes (because the H nucleus is light) so that electrical and mechanical anharmonicity become significant; the corresponding overtone transitions have relatively high intensity.

Highly excited vibrational states, such as those accessed in vibrational overtone spectroscopy, are of particular interest because of their relevance to the understanding of bond breaking and chemical transformation. When a molecule has a small amount of vibrational energy this energy is delocalized throughout the molecule, and the normal mode picture is appropriate. As we "warm the molecule up" to chemically significant energies, and give it more and more vibrational energy, the energy becomes localized in the weakest bond which eventually breaks. The normal mode picture is not appropriate at such high levels of vibrational excitation. Using a stationary state (time-independent) picture we would say that at high energies the vibrational states consist of a mixture of many harmonic oscillator (normal mode) basis states. However, to link the study of highly excited vibrational states with chemical transformations we need to use a time-dependent picture. This is where the concept of *internal vibrational redistribution* (IVR) enters. We picture IVR as the process whereby vibrational excitation initially localized in one, or a set, of normal modes, or alternatively in one, or a set, of bonds (neither situation being a stationary state) redistributes itself with the passage of time. Often the initial state is a *zero order bright state* produced by pulsed laser excitation. Because of its relevance to chemistry the study of IVR is a large field. It is clear that it is mainly through the use of the experimental and theoretical techniques of high resolution spectroscopy that we will be able to understand IVR to the extent necessary to predict and manipulate it.

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[9] See Eq. (4-7) for the definition of $\hat{O}_i$.

In the Bibliographical Notes we give examples of work on vibrational overtone spectroscopy, highly excited vibrational states, and IVR.

14.2 MAGNETIC DIPOLE AND ELECTRIC QUADRUPOLE TRANSITIONS

A transition between the states $\Phi'_{\rm int}$ and $\Phi''_{\rm int}$ can occur with the (weak) absorption or emission of electromagnetic radiation even if the electric dipole line strength [Eq. (14-5)] is zero as long as the matrix element of the magnetic dipole moment operator or electric quadrupole moment operator is nonvanishing (higher multipole transitions are possible but have not been observed). In general magnetic dipole and electric quadrupole transition probabilities are about 10^{-5} and 10^{-8}, respectively, of electric dipole transition probabilities. Such transitions are called forbidden since they are forbidden as electric dipole transitions.

The transition probability of a magnetic dipole transition from an initial state with the energy E'' to a final state with the energy E' involves matrix elements $\langle\Phi'_{\rm int}|d_A|\Phi''_{\rm int}\rangle$ of the space fixed magnetic dipole moment components d_A, where $A = \xi, \eta, \zeta$. The integrated absorption coefficient for a magnetic dipole transition is obtained from Eq. (14-3) by changing c to c^3 in the denominator, and μ_A to d_A in the expression for the line strength [see, for example, Eqs. (8) and (13) in Section 5^4 of Condon and Shortley (1963) which are expressions for the transition probabilities; these are proportional to the integrated absorption coefficients.[10]]. Thus for the states $\Phi'_{\rm int}$ and $\Phi''_{\rm int}$ to be connected by magnetic dipole radiation we must have

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[10] Equation (14-101) below is in SI units. In older texts (including Edition 1) the mixed (or Gaussian) system of units is used, and in that system electromagnetic units (emu) are used for magnetic quantities. In emu a 'c' appears in the denominator of the expression for the magnetic dipole moment. Condon and Shortley (1963) use emu for the magnetic dipole moment [see Eq. (9) of Section 4^4], and this is why we require this extra c^2 factor in the denominator for the integrated absorption coefficient of a magnetic dipole transition in relation to their expressions.

$$\langle \Phi'_{\rm int}|d_A|\Phi''_{\rm int}\rangle \neq 0 \tag{14-100}$$

for at least one of the A values ξ, η, or ζ. The ζ component of the magnetic dipole moment operator is given by

$$d_\zeta = \sum_j \frac{e_j}{2m_j}(\hat{l}_{j\zeta} + g_j \hat{s}_{j\zeta}), \tag{14-101}$$

where $\hat{l}_{j\zeta}$ is the ζ component of the orbital angular momentum of particle j given by

$$\hat{l}_{j\zeta} = -i\hbar\left(\xi_j\frac{\partial}{\partial\eta_j} - \eta_j\frac{\partial}{\partial\xi_j}\right), \tag{14-102}$$

and $\hat{s}_{j\zeta}$ ($= \hat{I}_{j\zeta}$ for a nucleus) is the ζ component of the spin angular momentum of particle j. The ξ and η components of the magnetic dipole moment operator can be obtained from Eqs. (14-101) and (14-102) by cyclic permutation of the symbols ξ, η and ζ. For each electron $g_j = g \approx 2$ [see, for example, Moss (1973)]. The magnetic dipole moment operator can be expressed in terms of the angular momenta $\hat{\boldsymbol{N}}$, $\hat{\boldsymbol{S}}$ and $\hat{\boldsymbol{I}}$. In their treatment of the Zeeman effect (see below) Bowater, Brown, and Carrington (1973) use a magnetic dipole moment operator consistent with the expression

$$\boldsymbol{d} = -g\mu_B\hat{\boldsymbol{S}} + \mu_B\,\mathbf{g}_l\hat{\boldsymbol{S}} - \mu_B\,\mathbf{g}_r\hat{\boldsymbol{N}} + g_N\,\mu_N\,\hat{\boldsymbol{I}}, \tag{14-103}$$

where μ_B is the Bohr magneton, μ_N is the nuclear magneton, and g_N is a nuclear g-factor [see, for example, Moss (1973)]. In Eq. (14-103), the operator triples $\boldsymbol{d}$, $\hat{\boldsymbol{S}}$, $\hat{\boldsymbol{N}}$, and $\hat{\boldsymbol{I}}$ are to be understood as three-component column vectors, and $\mathbf{g}_l$ and $\mathbf{g}_r$ are 3×3 matrices with elements depending on the electronic and vibrational coordinates.

We can calculate the matrix elements of d_A [Eq. (14-100)] using exactly the same techniques as we employed for the matrix elements of the electric dipole moment components μ_A above. The three components of $\boldsymbol{d}$ span the irreducible representation $D^{(1)}$ in $\boldsymbol{K}$(spatial), and we can transform them into space fixed irreducible spherical tensor operators by means of the expression used for the electric dipole moment components in Eq. (14-13):

$$\begin{aligned} d_{\rm s}^{(1,\pm1)} &= [\mp d_\xi + i d_\eta]/\sqrt{2} \\ d_{\rm s}^{(1,0)} &= d_\zeta. \end{aligned} \tag{14-104}$$

The molecule fixed irreducible spherical tensor operators $d_{\rm m}^{(1,\sigma)}$ are obtained from equations similar to Eq. (14-14), and the operators $d_{\rm s}^{(1,\sigma)}$ and $d_{\rm m}^{(1,\sigma)}$ will satisfy Eq. (14-15) with μ replaced by d. Hence, in calculating the transition probabilities of magnetic dipole transitions we can proceed exactly as described for electric dipole transitions in Eqs. (14-18)-(14-50). However, the magnetic dipole moment operators differ from the electric dipole moment operators in one important respect: they depend explicitly on the electron and nuclear spins [Eq. (14-103)]. Hence there is no purpose in evaluating the transition probabilities of magnetic dipole transitions in the approximation of a completely separable wavefunction where the effects of the electron and nuclear spins are neglected. If we take into account the contributions to $\hat{\boldsymbol{d}}$ from electron *and* nuclear spin the transition probabilities must be derived in terms of the fully coupled wavefunctions given by Eq. (13-221), and the result will be an expression which is analogous to, but [because of the four individual terms in Eq. (14-103)] considerably lengthier than, Eq. (14-50). This expression can be obtained from Eqs. (34)-(36) of Bowater, Brown, and Carrington (1973). It contains vibronic matrix elements of the molecule fixed components of $\boldsymbol{d}$, and these matrix elements can be analyzed in terms of the vanishing integral rule.

The operator d_A is invariant to any operation of the MS group (it transforms like $\hat{J}_A$) and so for fully coupled wavefunctions the rigorous magnetic dipole transition selection rules derived from the MS group are

$$\Gamma'_{\mathrm{int}} \otimes \Gamma''_{\mathrm{int}} \supset \Gamma^{(s)}. \qquad (14\text{-}105)$$

If the inversion operation E^* is contained in the MS group, or if we are using the CNPI group for classifying the molecular states, this can be expressed as a condition on the parities of the initial and final wavefunctions as

$$+ \leftrightarrow +, \quad - \leftrightarrow -, \quad \text{and} \quad + \not\leftrightarrow -. \qquad (14\text{-}106)$$

As mentioned above, the operator triple $\hat{\boldsymbol{d}}$ transforms as $D^{(1)}$ in $\boldsymbol{K}$(spatial) so the selection rule on F is

$$\Delta F = 0, \pm 1 \qquad (F' = 0 \not\leftrightarrow F'' = 0). \qquad (14\text{-}107)$$

As a result of the fact that the masses of the particles occur in Eq. (14-101) we see that the terms involving the orbital and spin magnetic moments of the electrons will be about 10^3 times larger than the terms involving the orbital and spin magnetic moments of the nuclei. Magnetic dipole transitions involving a reorientation of the electron orbital or spin magnetic moment have been known for a long time [see, for example, Herzberg (1946), Herzberg and Herzberg (1947), Babcock and Herzberg (1948), Arpigny (1966), Brown, Cole, and Honey (1972), and Zink and Mizushima (1987)]. For such transitions, we can neglect the contribution to $\hat{\boldsymbol{d}}$ from the nuclear spin and obtain the transition probabilities in terms of the wavefunctions given by Eq. (13-219); in this case we obtain a result analogous to Eq. (14-48). Again, the vibronic matrix elements can be analyzed in terms of the vanishing integral rule. Magnetic dipole rotation-vibration transitions can provide useful information that complements the information obtained from the electric dipole rotation-vibration spectrum of a molecule. Such transitions, belonging to the fundamental band of O_2, have been identified in stratospheric spectra [Dang-Nhu, Zander, Goldman, and Rinsland (1990)]. Note that NMR transitions are magnetic dipole transitions driven by nuclear spin magnetic moments.

Allowed electric quadrupole transitions involve the matrix element of the electric quadrupole moment of the molecule. The electric quadrupole moment components associated with the space fixed axes ξ, η, or ζ are given by

$$Q_{AB} = \sum_j e_j^2 \left(A_j B_j - \delta_{AB} \left[\xi_j^2 + \eta_j^2 + \zeta_j^2\right]/3\right) \tag{14-108}$$

where A, $B = \xi, \eta$, or ζ, A_j (B_j) is the A (B) coordinate of particle j, and j runs over all nuclei and electrons. Obviously, Q_{AB} is unchanged by the permutation of nuclei (since identical nuclei have the same charge) and by the inversion which takes A_j and B_j into $-A_j$ and $-B_j$, respectively. That is, Q_{AB} belongs to the totally symmetric irreducible representation $\Gamma^{(s)}$ in the MS group. From the nine Q_{AB} components we can form the following nine irreducible spherical tensor operators:

$$Q_s^{(0,0)} = -\frac{1}{\sqrt{3}}\left[Q_{\xi\xi} + Q_{\eta\eta} + Q_{\zeta\zeta}\right], \tag{14-109}$$

$$Q_s^{(1,\pm1)} = \frac{1}{2}\left[-Q_{\xi\zeta} + Q_{\zeta\xi} \mp i\left(Q_{\eta\zeta} - Q_{\zeta\eta}\right)\right], \tag{14-110}$$

$$Q_s^{(1,0)} = \frac{1}{\sqrt{2}}\, i\left[Q_{\xi\eta} - Q_{\eta\xi}\right], \tag{14-111}$$

$$Q_s^{(2,\pm2)} = \frac{1}{2}\left[Q_{\xi\xi} - Q_{\eta\eta} \pm i\left(Q_{\xi\eta} - Q_{\eta\xi}\right)\right], \tag{14-112}$$

$$Q_s^{(2,\pm1)} = \frac{1}{2}\left[\mp\left(Q_{\xi\zeta} + Q_{\zeta\xi}\right) - i\left(Q_{\eta\zeta} + Q_{\zeta\eta}\right)\right], \tag{14-113}$$

$$Q_s^{(2,0)} = \frac{1}{\sqrt{6}}\left[2Q_{\zeta\zeta} - Q_{\xi\xi} - Q_{\eta\eta}\right]. \tag{14-114}$$

However it is easy to show from Eq. (14-108) that the Q tensor is traceless, i.e., $Q_{\xi\xi} + Q_{\eta\eta} + Q_{\zeta\zeta} = 0$, so that the operator $Q_s^{(0,0)}$ in Eq. (14-109) vanishes. Further, for $A \neq B$ we have from Eq. (14-108) that $Q_{AB} = Q_{BA}$, and therefore the operators $Q_s^{(1,\sigma)}$ ($\sigma = 0, \pm1$) in Eqs. (14-110)-(14-111) vanish. Only the operators $Q_s^{(2,\sigma)}$ ($\sigma = 0, \pm1, \pm2$) in Eqs. (14-112)-(14-114) are nonzero, and they transform as $D^{(2)}$ in $\mathbf{K}$(spatial). From the transformation properties of the Q_{AB} components in the MS group and in $\mathbf{K}$(spatial) we derive the following rigorous selection rules for allowed electric quadrupole transitions

$$\Gamma'_{\text{int}} \otimes \Gamma''_{\text{int}} \supset \Gamma^{(s)}, \qquad \text{i.e.,} \qquad + \leftrightarrow +, \quad - \leftrightarrow -, \quad \text{and} \quad + \not\leftrightarrow -, \tag{14-115}$$

and from Eq. (7-45)

$$\Delta F = 0, \pm1, \pm2 \qquad (F' + F'' \geq 2). \tag{14-116}$$

From Eq. (7) of Section 6^4 of Condon and Shortley (1963), the expression for the integrated absorption coefficient of an electric quadrupole transition is given by Eq. (14-3) where we replace $8\pi^3 N_A \tilde{\nu}_{if}$ by $4\pi^5 N_A \tilde{\nu}_{if}^3$ in the numerator, and 3 by 5 in the denominator; we also replace μ_A by Q_{AB} (and introduce a double sum over A and B) in the expression for the linestrength [Eq. (14-5)].

The selection rules are obtained by introducing in irreducible spherical tensor notation a quantity analogous to the line strength given in Eq. (14-17):

$$P(f \leftarrow i) = \sum_{\Phi'_{\rm int}, \Phi''_{\rm int}} \sum_{\sigma=-2}^{2} \left| \left\langle \Phi'_{\rm int} \left| Q_{\rm s}^{(2,\sigma)} \right| \Phi''_{\rm int} \right\rangle \right|^2 , \qquad (14\text{-}117)$$

where the operators $Q_{\rm s}^{(2,\sigma)}$ are given by Eqs. (14-112)-(14-114). We form molecule fixed irreducible spherical tensor operators $Q_{\rm m}^{(2,\sigma)}$ by replacing (ξ, η, ζ) by (x, y, z) on the right hand sides in Eqs. (14-112)-(14-114). The two sets of operators $Q_{\rm s}^{(2,\sigma)}$ ($\sigma = 0, \pm 1, \pm 2$) and operators $Q_{\rm m}^{(2,\sigma')}$ ($\sigma' = 0, \pm 1, \pm 2$) will satisfy Eq. (14-16) for $\omega = 2$. The matrix elements entering into Eq. (14-117) can be derived using exactly the same techniques as we employ for electric dipole moment intensities. For example, in the approximation of a completely separable wavefunction we obtain a result virtually identical to Eq. (14-33):

$$\begin{aligned} P(f \leftarrow i) = {} & g_{\rm ns} (2S+1)(2N''+1)(2N'+1) \\ & \times \left| \sum_{k'=-N'}^{N'} \sum_{k''=-N''}^{N''} c_{k'}^{(N')*} c_{k''}^{(N'')} \right. \\ & \left. \times (-1)^{k'} \sum_{\sigma'=-2}^{2} \left\langle \Phi'_{\rm vib} \left| Q_{\rm m}^{(2,\sigma')}(e', e'') \right| \Phi''_{\rm vib} \right\rangle \begin{pmatrix} N'' & 2 & N' \\ k'' & \sigma' & -k' \end{pmatrix} \right|^2 , \end{aligned} \qquad (14\text{-}118)$$

where the vibronic matrix elements are defined by analogy with the definitions for electric dipole transitions. From the properties of the $3j$-symbol we derive that the transition probability will vanish unless

$$\Delta N = 0, \pm 1, \pm 2 \quad (N' + N'' \geq 2). \qquad (14\text{-}119)$$

Transitions with $\Delta N = -1$, 0 and $+1$ said to belong to the P branch, Q branch and R branch, respectively, exactly as for electric dipole transitions. The additional transitions allowed here with $\Delta N = -2$ and $+2$ are called O branch transitions and S branch transitions, respectively. Further vibronic selection rules (and selection rules on k determined from the condition $\sigma' = k' - k''$) can be obtained by analyzing the vibronic matrix elements in terms of the vanishing integral rule. In this analysis, we can use the fact that the molecule fixed components of the electric quadruple moment $Q_{\beta\gamma}$ (where $\beta, \gamma = x, y, z$) belong to the same irreducible representation of the MS group as the electric polarizability component $\alpha_{\beta\gamma}$ [see Eq. (14-138) that follows] and these species are given in the character tables in Appendix ***A***. Thus electric quadrupole transitions occur between vibronic states whose species are connected by the species of a component of the electric polarizability tensor.

The most famous example of an electric quadrupole rotation-vibration spectrum is that of the hydrogen molecule [Herzberg (1949, 1950)]; the S(0) [$N = J = 2 \leftarrow 0$] line of the $v = 1 \leftarrow 0$ fundamental is shown here in Fig 16-2 on page 577. Reid, Sinclair, Robinson, and McKellar (1981) made the the first observation of quadrupole rotation-vibration transitions in a molecule other than hydrogen; they measured the electric quadrupole $S(5)$ [$N = 7 \leftarrow 5$] and $S(7)$ [$N = 9 \leftarrow 7$] transitions in the $v = 1 \leftarrow 0$ band of $^{16}O_2$. Electric quadrupole transitions in the $v = 1 \leftarrow 0$ band of atmospheric N_2 have been observed by Camy-Peyret, Flaud, Delbouille, Roland, Brault, and Testerman (1981), and by Goldman, Reid, and Rothman (1981), and of laboratory N_2 by Reuter, Jennings, and Brault (1986).

14.3 MULTIPHOTON PROCESSES AND THE RAMAN EFFECT

The selection rules for multiphoton processes, such as occur in Raman scattering, can be obtained by expressing the intensity of the multiphoton process as the sum of products of one-photon electric dipole matrix elements. For example, a two-photon transition from a state i to a state f can take place only if there exists some third state j such that both transitions $j \leftarrow i$ and $f \leftarrow j$ are electric dipole allowed. If states i and f are such that there are no states j for which both $j \leftarrow i$ and $f \leftarrow j$ are electric dipole allowed then the transition $f \leftarrow i$ is forbidden as a two-photon process. The strict selection rules [obtained from the strict one-photon selection rules of Eqs. (14-8)-(14-11)] are that the transition between the states Φ''_{int} and Φ'_{int} is forbidden as an n-photon electric dipole transition unless

$$\Gamma'_{\text{int}} \otimes \Gamma''_{\text{int}} \supset [\Gamma^*]^n \tag{14-120}$$

and[11]

$$\Delta F = 0, \pm 1, \pm 2, \dots, \pm n. \tag{14-121}$$

Since

$$[\Gamma^*]^n = \Gamma^{(s)} \qquad \text{if } n \text{ is even} \tag{14-122}$$

and

$$[\Gamma^*]^n = \Gamma^* \qquad \text{if } n \text{ is odd,} \tag{14-123}$$

then for n even we have $+ \leftrightarrow +$, $- \leftrightarrow -$, and $+ \not\leftrightarrow -$ whereas for n odd we have $+ \leftrightarrow -$, $+ \not\leftrightarrow +$, and $- \not\leftrightarrow -$. Further selection rules on the electronic, and vibrational symmetries, and on the vibrational and rotational quantum numbers, can be obtained from the one-photon selection rules previously discussed.

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[11] **Where there is the further restriction $F' + F'' \geq n$.**

In Raman scattering radiation of wavenumber $\tilde{\nu}$ (usually visible light) is incident on a molecule that is in a state i with energy E''. Scattered radiation of wavenumber $\tilde{\nu} - \tilde{\nu}_{if}$ is detected, where $hc\tilde{\nu}_{if} = E' - E''$, and the molecule undergoes a two-photon transition to the state f (whose energy E' can be above or below the energy E'' of the state i). The intensity of the scattered radiation in the Raman effect [Placzek (1934)] depends on the intensity of the incident radiation, on the wavenumber $\tilde{\nu} - \tilde{\nu}_{if}$, and on the square of the two-photon transition moment $\boldsymbol{C}_{if}^{B}$, where $\boldsymbol{C}_{if}^{B}$ has components C_{if}^{AB} ($A = \xi, \eta, \text{or } \zeta$) given by [see, for example, Mills (1964b), Eq. (2)]

$$C_{if}^{AB} = \sum_{j} \left[\frac{\mu_{ij}^{B}\mu_{jf}^{A}}{hc\,(\tilde{\nu}_{ji} - \tilde{\nu})} + \frac{\mu_{ij}^{A}\mu_{jf}^{B}}{hc\,(\tilde{\nu}_{jf} + \tilde{\nu})} \right], \qquad (14\text{-}124)$$

where B is the direction of polarization of the electric vector of the incident radiation (i.e., $B = \xi, \eta, \text{or } \zeta$) and, for example, μ_{ij}^{A} is the electric dipole matrix element

$$\mu_{ij}^{A} = \left\langle \Phi_{\text{int}}^{(i)} \left| \mu_{A} \right| \Phi_{\text{int}}^{(j)} \right\rangle \qquad (14\text{-}125)$$

with the wavefunctions $\Phi_{\text{int}}^{(i)}$ and $\Phi_{\text{int}}^{(j)}$ describing the states i and j, respectively. Usually the states i and f are different rotation-vibration levels of the ground electronic state of the molecule, $\tilde{\nu} \gg |\tilde{\nu}_{if}|$, and excited electronic states (j) are beyond the reach of visible light with $\tilde{\nu} \ll \tilde{\nu}_{ji}$. In these circumstances more restrictive selection rules for $f \leftarrow i$ to be allowed in the Raman effect, over and above those derived by considering the selection rules for the successive electric dipole transitions $j \leftarrow i$ and $f \leftarrow j$, can be derived. This approximation is called the ***polarizability approximation***.

The polarizability approximation is only applicable if

- i and f are ground electronic state rotation-vibration states,
- the Born-Oppenheimer separation is valid for these states and for the intermediate states j,
- $\tilde{\nu} \ll \tilde{\nu}_{ji}$ and $\tilde{\nu} \ll \tilde{\nu}_{jf}$ so that we can satisfactorily approximate $\tilde{\nu}_{ji} - \tilde{\nu} \to \tilde{\nu}_{ji}$ and $\tilde{\nu}_{jf} + \tilde{\nu} \to \tilde{\nu}_{jf}$, and
- we can neglect the dependence of the wavenumbers $\tilde{\nu}_{ji}$ and $\tilde{\nu}_{jf}$ on the rotation-vibration state.

In this case, we can write the intermediate wavefunction $\Phi_{\text{int}}^{(j)}$ as

$$\Phi_{\text{int}}^{(j)} = \Phi_{\text{nspin}}^{(j)}\, \Phi_{\text{rv}}^{(j)} \Phi_{\text{elec}}^{(e_j,S,m_S)}, \qquad (14\text{-}126)$$

with similar expressions for the wavefunctions of the i and f states, and we can approximate the energy denominators in Eq. (14-124) as

$$hc\,(\tilde{\nu}_{ji} - \tilde{\nu}) = hc\,(\tilde{\nu}_{jf} + \tilde{\nu}) = E_{\text{elec}}^{(j)} - E_{\text{elec}}^{(0)}, \qquad (14\text{-}127)$$

where the quantity on the right hand side is the difference in electronic energy [see Eq. (9-61)] between the excited electronic state j and the electronic ground state. In the polarizability approximation the quantity C_{if}^{AB} in Eq. (14-124) can be written as

$$C_{if}^{AB} \approx \langle \Phi_{\mathrm{rv}}'' | \alpha_{AB} | \Phi_{\mathrm{rv}}' \rangle, \tag{14-128}$$

where Φ_{rv}'' and Φ_{rv}' are the rotation-vibration wavefunctions of the i and f states, respectively. The quantity α_{AB} (A, $B = \xi$, η, or ζ) in Eq. (14-128) is a space fixed component of the ***static electric polarizability tensor*** given by

$$\begin{aligned}\alpha_{AB} = \sum_j \Bigg[& \frac{\left\langle \Phi_{\mathrm{elec}}^{(e_0,S,m_S)} | \mu_B | \Phi_{\mathrm{elec}}^{(e_j,S,m_S)} \right\rangle \left\langle \Phi_{\mathrm{elec}}^{(e_j,S,m_S)} | \mu_A | \Phi_{\mathrm{elec}}^{(e_0,S,m_S)} \right\rangle}{E_{\mathrm{elec}}^{(j)} - E_{\mathrm{elec}}^{(0)}} \\ & + \frac{\left\langle \Phi_{\mathrm{elec}}^{(e_0,S,m_S)} | \mu_A | \Phi_{\mathrm{elec}}^{(e_j,S,m_S)} \right\rangle \left\langle \Phi_{\mathrm{elec}}^{(e_j,S,m_S)} | \mu_B | \Phi_{\mathrm{elec}}^{(e_0,S,m_S)} \right\rangle}{E_{\mathrm{elec}}^{(j)} - E_{\mathrm{elec}}^{(0)}} \Bigg],\end{aligned} \tag{14-129}$$

where $\Phi_{\mathrm{elec}}^{(e_0,S,m_S)}$ is the electronic wavefunction for the electronic ground state. In obtaining Eqs. (14-128) and (14-129) we have used the fact that the nuclear spin functions are normalized [see Eqs. (14-29)-(14-30)], and we have summed out the rotation-vibration parts of the wavefunction for the intermediate state j. This is permissible since these states form a complete basis set for rotation and vibration. The sum in Eq. (14-129) is over the excited electronic states only.

The polarizability tensor relates the induced dipole moment components P_{A} in a molecule to the electric vector components E_{B} of the incident radiation according to

$$P_{\mathrm{A}} = \sum_{B=\xi,\eta,\zeta} \alpha_{AB} E_{\mathrm{B}}. \tag{14-130}$$

In the polarizability approximation the intensity of a rotation-vibration transition in the Raman effect, within a nondegenerate ground electronic state, is given by the values of matrix elements of the space fixed components of the polarizability tensor, and so a Raman transition with a nonvanishing transition probability will satisfy

$$\langle \Phi_{\mathrm{rv}}' | \alpha_{AB} | \Phi_{\mathrm{rv}}'' \rangle \neq 0 \tag{14-131}$$

with A, $B = \xi$, η, or ζ.

The matrix elements in Eq. (14-131) can be derived by transforming the tensor components α_{AB} to irreducible spherical tensor form. This is done by replacing Q by α in Eqs. (14-109)-(14-114). The static electric polarizability tensor is symmetric but not traceless, so Eqs. (14-109)-(14-114) produce a total of six irreducible spherical tensor operators, $\alpha_{\mathrm{s}}^{(0,0)}$ and $\alpha_{\mathrm{s}}^{(2,\sigma)}$ ($\sigma = 0, \pm 1,$

± 2). The operator $\alpha_s^{(0,0)}$ transforms as $D^{(0)}$ (i.e., the totally symmetric representation) in $\boldsymbol{K}$(spatial), and the operators $\alpha_s^{(2,\sigma)}$ transform as $D^{(2)}$. The total transition probability for a Raman transition is proportional to a transition moment square, $R(f \leftarrow i)$, which can be shown to depend on the two quantities,

$$R_0(f \leftarrow i) = \left|\left\langle \Phi'_{\rm rv} \left| \alpha_s^{(0,0)} \right| \Phi''_{\rm rv} \right\rangle\right|^2 . \tag{14-132}$$

and

$$R_2(f \leftarrow i) = \sum_{\sigma=-2}^{2} \left|\left\langle \Phi'_{\rm rv} \left| \alpha_s^{(2,\sigma)} \right| \Phi''_{\rm rv} \right\rangle\right|^2 . \tag{14-133}$$

We say that $R_0(f \leftarrow i)$ determines the transition probability for *isotropic Raman scattering*, and $R_2(f \leftarrow i)$ determines the probability for *anisotropic Raman scattering*. The extent to which isotropic and anisotropic Raman scattering will contribute to the total transition moment square $R(f \leftarrow i)$ depends on the angle between the electric field vectors of the incident light and the scattered light, i.e., on the experimental setup. For example, if the two electric field vectors are parallel we have [Brodersen (1979)]

$$R(f \leftarrow i) = 10\, R_0(f \leftarrow i) + 4\, R_2(f \leftarrow i), \tag{14-134}$$

whereas if the two vectors form an angle of 90°

$$R(f \leftarrow i) = 3\, R_2(f \leftarrow i). \tag{14-135}$$

In order to obtain the selection rules for isotropic and anisotropic Raman scattering we introduce molecule fixed irreducible spherical tensor operators $\alpha_m^{(\omega,\sigma)}$ by replacing the space fixed tensor components α_{AB} (A, $B = \xi$, η, or ζ) by molecule fixed components $\alpha_{\delta\gamma}$ (δ, $\gamma = x$, y, or z) in the expressions obtained from Eqs. (14-109)-(14-114). For isotropic Raman scattering, we simply have $\alpha_m^{(0,0)} = \alpha_s^{(0,0)}$ because $\alpha_s^{(0,0)}$ is totally symmetric in $\boldsymbol{K}$(spatial) and thus invariant under rotations in space. In the approximation of a completely separable wavefunction, we derive (cf. Eq. (14-33))

$$R_0(f \leftarrow i) = g_{\rm ns}\,(2S+1)(2N''+1) \times \left|\left\langle \Phi'_{\rm vib} \left| \alpha_m^{(0,0)}(e'', e'') \right| \Phi''_{\rm vib} \right\rangle\right|^2 \left|\langle \Phi'_{\rm rot} | \Phi''_{\rm rot} \rangle\right|^2 . \tag{14-136}$$

In order for $R_0(f \leftarrow i)$ not to vanish, we must have $\Phi'_{\rm rot} = \Phi''_{\rm rot}$ so that $N' = N''$. Furthermore, the operator $\alpha_m^{(0,0)}$ is always totally symmetric in the MS group. Thus, in the nondegenerate ground electronic state we consider here $\alpha_m^{(0,0)}$ is also totally symmetric in the MS group, and the vanishing integral rule applied to the vibronic integral in Eq. (14-136) produces the selection rule

$$\Gamma'_{\rm vib} = \Gamma''_{\rm vib} \tag{14-137}$$

for isotropic Raman scattering.

The quantity $R_2(f \leftarrow i)$ is obtained in a manner identical to the derivation of $P(f \leftarrow i)$ [Eq. (14-118)] the transition probability for electric quadrupole transitions. In the approximation of a completely separable wavefunction we can take $R_2(f \leftarrow i)$ to be given by the right hand side of Eq. (14-118) if we replace $Q_{\mathrm{m}}^{(2,\sigma')}(e', e'')$ by $\alpha_{\mathrm{m}}^{(2,\sigma')}(e'', e'')$. Because of this, and because as mentioned above, the molecule fixed component $\alpha_{\delta\gamma}$ ($\delta, \gamma = x, y$, or z) of the static electric polarizability tensor transforms under the operations in the MS group exactly as the component $Q_{\delta\gamma}$ of the electric quadrupole moment, transitions resulting from anisotropic Raman scattering obey the same selection rules as electric quadrupole transitions. In particular, anisotropic Raman scattering gives rise to O, P, Q, R and S branch transitions.

The molecule fixed component $\alpha_{\delta\gamma}$ ($\delta, \gamma = x, y$, or z) of the static electric polarizability has the same symmetry as

$$\left\langle \Phi_{\mathrm{elec}}^{(e'',S'',m_S'')} \middle| \left(\sum_m e^2 \gamma_m \delta_m \right) \middle| \Phi_{\mathrm{elec}}^{(e'',S'',m_S'')} \right\rangle, \tag{14-138}$$

where m runs over all the electrons in the molecule. Since the polarizability tensor is symmetric there are six independent $\alpha_{\delta\gamma}$ components, and they transform like the symmetrized square of the representation of the MS group generated by the electric dipole moment operator components μ_x, μ_y and μ_z. The allowed transitions are more restricted by demanding Eq. (14-131) to be nonvanishing than by demanding Eq. (14-124) to be nonvanishing [see, for example, Mills (1964b)]. In order for Eq. (14-131) to be nonvanishing the product of the vibrational species, $\Gamma'_{\mathrm{vib}} \otimes \Gamma''_{\mathrm{vib}}$, must contain the symmetrized square of the species of the dipole moment operator components (μ_x, μ_y and μ_z). The vibrational part of Eq. (14-124) is nonvanishing if the product of the vibrational species contains the complete square of the species of (μ_x, μ_y and μ_z). For example, in a $\boldsymbol{C}_{3\mathrm{v}}$ molecule μ_x, μ_y and μ_z transform as $A_1 \oplus E$ the square of which is $2A_1 \oplus A_2 \oplus 3E$, and the symmetrized square of which is $2A_1 \oplus 2E$. Using polarizability theory a vibrational transition of the type $A_2 \leftarrow A_1$ would be forbidden in the Raman effect whereas using the less approximate theory demanding that Eq. (14-124) be nonvanishing this transition would be allowed in the Raman effect ($A_2 \leftarrow E \leftarrow A_1$ are both dipole allowed). The polarizability approximation is a very good one in practice when the criteria for its applicability ($\tilde{\nu} \gg |\tilde{\nu}_{if}|$, and $hc\tilde{\nu}$ much less than the electronic excitation energies) are satisfied.

The species of the polarizability tensor components $\alpha_{\delta\gamma}$ are the same as the species of the products ($T_\delta T_\gamma$) and these species are indicated in the MS tables in Appendix ***A***. A vibrational transition will be Raman active if the vibrational species are connected by the species of a polarizability tensor component. We can expand the electronic polarizability tensor as a Taylor series in the normal coordinates in the same way that $\mu_\alpha(e', e'')$ is expanded in Eq. (14-41). As a result the most intense vibrational Raman bands that can be excited from the ground vibrational state will be the fundamentals (for which $\Delta v_r = 1$)

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and each Raman active state must have a normal coordinate that transforms like a component of the polarizability tensor. In centrosymmetric molecules the polarizability tensor is of g symmetry (it is the product of two T_α which are u) and only fundamental bands involving g vibrations can be active. This is in contrast to the infrared active fundamentals which must be u. Thus in centrosymmetric molecules there is an exclusion principle that no fundamental band can be simultaneously infrared and Raman active. The determination of the number of infrared and Raman active fundamentals in a rigid molecule is a great help in determining its symmetry in the equilibrium configuration.

14.4 THE ZEEMAN EFFECT

In the Zeeman effect a homogeneous magnetic field $\boldsymbol{B}$ is applied to the molecule under study. Choosing the ζ axis to be along $\boldsymbol{B}$, the field free molecular Hamiltonian is augmented by the term [see, for example, Chapter 11 in Townes and Schawlow (1955)]

$$\hat{H}_{\mathrm{Zeeman}} = -d_\zeta B_\zeta = -d_{\mathrm{s}}^{(1,0)} B_\zeta \qquad (14\text{-}139)$$

where d_ζ is the ζ component of the magnetic dipole moment operator for the molecule; see Eq. (14-101). From Eq. (14-103) we see that d_ζ involves both the orbital and spin angular momenta in the molecule. In the presence of the external magnetic field the molecular Hamiltonian becomes $\hat{H} = \hat{H}_{\mathrm{int}} + \hat{H}_{\mathrm{Zeeman}}$, where $\hat{H}_{\mathrm{int}}$ [Eq. (7-33)] is the Hamiltonian for the free molecule. We can generate the eigenvalues and eigenfunctions for $\hat{H}$ by constructing its matrix representation in a basis of eigenfunctions Φ_{int} for $\hat{H}_{\mathrm{int}}$. In this basis, the matrix representation of $\hat{H}_{\mathrm{int}}$ is obviously diagonal with the diagonal matrix elements equal to the energies of the molecule in field free space. Since B_ζ is a constant, the matrix elements of $\hat{H}_{\mathrm{Zeeman}}$ are proportional to the matrix elements

$$\langle \Phi'_{\mathrm{int}} | d_\zeta | \Phi''_{\mathrm{int}} \rangle = \langle \Phi'_{\mathrm{int}} | d_{\mathrm{s}}^{(1,0)} | \Phi''_{\mathrm{int}} \rangle \qquad (14\text{-}140)$$

which, as we have seen above, determine the intensities of magnetic dipole transitions in the field-free case. These matrix elements can be evaluated using the techniques discussed in this chapter [see Eqs. (34)-(36) of Bowater, Brown, and Carrington (1973)]. The Zeeman effect is discussed in Chapter 11 of Townes and Schawlow, and in Chapter 11 of Gordy and Cook (1984); we only discuss the symmetry aspects.

Table 14-2

The character table of the C_∞ group

	E	$2R_\zeta^\varepsilon$	$\cdots$
Σ:	1	1	$\cdots$
Π:	1	$e^{i\varepsilon}$	$\cdots$
	1	$e^{-i\varepsilon}$	$\cdots$
Δ:	1	$e^{2i\varepsilon}$	$\cdots$
	1	$e^{-2i\varepsilon}$	$\cdots$
Φ:	1	$e^{3i\varepsilon}$	$\cdots$
	1	$e^{-3i\varepsilon}$	$\cdots$
$\vdots$	$\vdots$	$\vdots$	$\cdots$

We are interested in knowing how the addition of $\hat{H}_{\text{Zeeman}}$ to the molecular Hamiltonian changes the energy levels and wavefunctions of the molecule from those obtained in field-free space. We can appreciate this qualitatively from the symmetry of $\hat{H}_{\text{Zeeman}}$ in the MS group and in the $\boldsymbol{K}$(spatial) group. Since identical particles have the same charge, mass, and spin, $\hat{H}_{\text{Zeeman}}$ is invariant to any permutation of identical particles. Also the inversion, which simultaneously changes the sign of all ξ_i, η_i, and ζ_i (but which does not affect the spins), will leave $\hat{H}_{\text{Zeeman}}$ invariant. Thus the term $\hat{H}_{\text{Zeeman}}$ is totally symmetric in the MS group. This means that $\hat{H}_{\text{Zeeman}}$ can only cause states of the same MS group symmetry to interact and that the Hamiltonian matrix (*including* Zeeman terms) can be factored into blocks by using the MS group symmetry species. The term $\hat{H}_{\text{Zeeman}}$ is not, however, totally symmetric in the group $\boldsymbol{K}$(spatial) but it is invariant to any rotation about the direction of $\boldsymbol{B}$ (the ζ direction in our example). The reader can see that twofold rotations about the ξ or η directions will change the sign of the orbital part of $\hat{H}_{\text{Zeeman}}$ but that any rotation about the ζ axis will leave it invariant. Thus the rotational symmetry is reduced to $\boldsymbol{C}_\infty$(spatial) and the $\boldsymbol{C}_\infty$ character table is given in Table 14-2. In the group $\boldsymbol{C}_\infty$(spatial) the molecular states span the representations Σ, Π, Δ etc., as $m_F = 0, \pm 1, \pm 2$, etc. (note that the Π, Δ, etc., representations are separably degenerate), and F does not remain a good quantum number. In the presence of a magnetic field time reversal symmetry is lost, since $\hat{H}_{\text{Zeeman}}$ is not invariant to the reversal of all momenta and spins, and separably degenerate states are not required by symmetry to be degenerate. As a result each level that in field free space is characterized by the quantum number F, with a $(2F+1)$-fold m_F-degeneracy, is split into $2F+1$ levels each of which has a definite m_F value and the same MS group symmetry label. In a weak field F would be a useful near quantum number and the most intense electric dipole transitions for the molecule would satisfy $\Delta F = 0, \pm 1$. The strictly allowed electric dipole transitions would be all those that satisfy $\Delta m_F = 0, \pm 1$ ($m''_F = 0 \nleftarrow m'_F = 0$) with MS group species connected by Γ^*.

In this section, we have investigated the transformation properties of $\hat{H}_{\text{int}} + \hat{H}_{\text{Zeeman}}$ separately for MS group operations and for operations in $\boldsymbol{K}$(spatial). A more systematic approach to this symmetry analysis has been employed by Watson (1975). He considers first the *zero field symmetry group* (or *ZFS group*)

$$\boldsymbol{G}^{\text{ZFS}} = \boldsymbol{K}(\text{spatial}) \otimes \boldsymbol{G}^{\text{MS}}, \tag{14-141}$$

where $\boldsymbol{G}^{\text{MS}}$ is the MS group. In the absence of external electric and magnetic fields, $\boldsymbol{G}^{\text{ZFS}}$ is the symmetry group of $\hat{H}_{\text{int}}$ associated with permutation-inversion and rotational symmetry [see Chapter 7]. Watson then determines the subgroup $\boldsymbol{G}^{\text{MFS}}$ [the *magnetic field symmetry group* (or *MFS group*)] of $\boldsymbol{G}^{\text{ZFS}}$ whose elements are symmetry operations also for $\hat{H}_{\text{int}} + \hat{H}_{\text{Zeeman}}$. It follows from the arguments of the preceding paragraph that

$$\boldsymbol{G}^{\text{MFS}} = \boldsymbol{C}_{\infty}(\text{spatial}) \otimes \boldsymbol{G}^{\text{MS}}. \tag{14-142}$$

In this situation, it is permissible to make the symmetry analysis separately for $\boldsymbol{C}_{\infty}$(spatial) and $\boldsymbol{G}^{\text{MS}}$ as we have already done [see Sections 5.8.2 and 6.3.1]. Thus, for an external magnetic field, the explicit consideration of the group $\boldsymbol{G}^{\text{MFS}}$ does not provide more information than that obtained in our discussion above.

14.5 THE STARK EFFECT

In the Stark effect a homogeneous electric field $\boldsymbol{E}$ is applied to the molecules under study. Choosing the ζ axis to be along $\boldsymbol{E}$, the field free molecular Hamiltonian is augmented by the term [see, for example, Chapter 10 in Townes and Schawlow (1955)]

$$\hat{H}_{\text{Stark}} = -\left(\sum_j e_j \zeta_j\right) E_\zeta = -\mu_\zeta E_\zeta = -\mu_{\text{s}}^{(1,0)} E_\zeta, \tag{14-143}$$

involving the space fixed component μ_ζ of the electric dipole moment operator. By analogy with the treatment of the Zeeman effect discussed above, we can obtain the eigenfunctions and eigenvectors of the total Hamiltonian $\hat{H} = \hat{H}_{\text{int}} + \hat{H}_{\text{Stark}}$ by diagonalizing its matrix representation in a basis of eigenfunctions Φ_{int} for $\hat{H}_{\text{int}}$. The central problem in determining the elements of this matrix representation is to evaluate $\langle \Phi'_{\text{int}} | \mu_\zeta | \Phi''_{\text{int}} \rangle = \langle \Phi'_{\text{int}} | \mu_{\text{s}}^{(1,0)} | \Phi''_{\text{int}} \rangle$. These are the matrix elements determining the intensities of electric dipole transitions. Thus the Stark effect mixes those states between which electric dipole transitions are allowed. Note that $\hat{H}_{\text{Stark}}$ is invariant to time reversal (unlike $\hat{H}_{\text{Zeeman}}$) since it is unaffected by the reversal of momenta and spins. The matrix elements of $\hat{H}_{\text{Stark}}$ are given in Eq. (37) of Bowater, Brown, and Carrington (1973). The measurement of Stark shifts is the most precise way of determining the dipole moment of a molecule [see Eq. (14-85) for the definition of the dipole moment]. The Stark effect is discussed in Chapter 10 of Townes and Schawlow (1975), in

Chapter 10 of Gordy and Cook (1984), and in Chapter 7 of Kroto (1992); we will concentrate on the symmetry aspects.

For the electric fields used in Stark shift measurements perturbation theory is usually sufficient to account for the effect, and first order Stark shifts are the most significant. Watson (1974) deduces the symmetry condition on the rovibronic species Γ_{rve} of a level for it to have a first order Stark shift by using a general theorem concerning the matrix elements of operators between components of a degenerate state;[12] this general theorem is deduced by considering the effect of the time reversal symmetry operation. The symmetry condition is

$$\Gamma^{*} \subset \{\Gamma_{\text{rve}}^{2}\} \qquad (14\text{-}144)$$

where Γ^{*} is the electric dipole representation (the symmetry of μ_{ζ}), and $\{\Gamma_{\text{rve}}^{2}\}$ is the antisymmetric square of the rovibronic species [see Eq. (6-118)]. In order for this condition to be satisfied it is necessary (but not sufficient) that Γ_{rve} be degenerate. Further, for any E species of a general symmetric top $\{E^2\}$ is always the species of J_z, where z is the symmetry axis, and for any symmetric top molecule Γ^{*} is the species of J_zT_z (as discussed on page 418), so that Eq. (14-144) reduces to the requirement that T_z be totally symmetric, i.e., that the molecule be *polar*. The rotational energy levels of a nonpolar symmetric top molecule cannot have a first-order Stark shift except in the case of an appropriate accidental degeneracy. Watson (1974) shows that 'accidentally' degenerate *l*-doublet or *k*-doublet levels do not lead to a first order (or nearly first order) Stark shift in a nonpolar symmetric top molecule. Two examples illustrate the application of the rule: methyl fluoride and allene. For a $\boldsymbol{C}_{3\text{v}}$ molecule like methyl fluoride $\Gamma^{*} = A_2$ and for an E rovibronic level $\{E^2\} = A_2$, so a first order Stark shift is allowed. For a $\boldsymbol{D}_{2\text{d}}$ molecule like allene $\Gamma^{*} = B_1$ and for an E rovibronic level $\{E^2\} = A_2$, so a first order Stark shift is forbidden. Note that centrosymmetric molecules cannot satisfy Eq. (14-144), and thus the only point groups we need to consider for spherical top molecules are $\boldsymbol{T}$, $\boldsymbol{T}_{\text{d}}$, $\boldsymbol{O}$ and $\boldsymbol{I}$. Detailed examination using Eq. (14-144) shows that of these only the E levels of $\boldsymbol{T}$ or $\boldsymbol{T}_{\text{d}}$ molecules can have a first order Stark shift. In accordance with this symmetry rule first order Stark shifts are seen for E levels in the Stark spectrum of the nonpolar molecule methane [see Uehara, Sakurai, and Shimoda (1969), Luntz and Brewer (1971), Luntz (1971) and Ozier (1971)]. Application of these same ideas to the Zeeman effect shows that there is no symmetry restriction on a first order Zeeman shift [Watson (1974)].

We now turn to the consideration of the symmetry of H_{Stark}, and we make use of another paper by Watson (1975). The Hamiltonian $\hat{H}_{\text{int}} + \hat{H}_{\text{Stark}}$ of a molecule in an electric field is invariant to any permutation of identical nuclei but not to the inversion E^{*} (since $\hat{H}_{\text{Stark}}$ is changed in sign by E^{*}). We can write the MS group symbolically as

$$\boldsymbol{G}^{\text{MS}} = \left\{\boldsymbol{G}^{\text{PSMS}}, \boldsymbol{Q}^{*}\right\}, \qquad (14\text{-}145)$$

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[12] See also Chapter 13 on page 386.

where $\boldsymbol{G}^{\mathrm{PSMS}}$ is the permutation subgroup of the MS group (the PSMS group), and $\boldsymbol{Q}^*$ is the set of permutation-inversion operations in the MS group [$\boldsymbol{Q}^*$ is not a group since, for example, it contains no identity operation, and the product of any two operations in it is a permutation and belongs to $\boldsymbol{G}^{\mathrm{PSMS}}$]. Molecular symmetry group elements belonging to $\boldsymbol{G}^{\mathrm{PSMS}}$ leave $H_{\mathrm{int}} + H_{\mathrm{Stark}}$ unchanged, but elements in $\boldsymbol{Q}^*$ leave only H_{int} unchanged and reverse the sign of H_{Stark}.

The $\boldsymbol{K}$(spatial) symmetry is spoiled by H_{Stark}, and F is no longer a good quantum number. However, the Stark Hamiltonian is invariant to the operations of the $\boldsymbol{C}_\infty$(spatial) group, where the rotations are about the field direction. Rotations of π about arbitrary axes in the $\xi\eta$ plane [i.e., axes perpendicular to the direction of the electric field] leave H_{int} invariant but reverse the sign of H_{Stark}.

We follow Watson (1975) in determining the subgroup $\boldsymbol{G}^{\mathrm{EFS}}$ [the *electric field symmetry group* (or *EFS group*)] of $\boldsymbol{G}^{\mathrm{ZFS}}$ [see Eq. (14-141)]. The EFS group contains the symmetry operations of the Stark Hamiltonian $\hat{H}_{\mathrm{int}} + \hat{H}_{\mathrm{Stark}}$, i.e., all operations obtained by combining

- an arbitrary rotation from the group $\boldsymbol{C}_\infty$(spatial) [i.e., a rotation about the field direction] with an arbitrary permutation of identical nuclei from $\boldsymbol{G}^{\mathrm{PSMS}}$, or
- an arbitrary rotation from $\boldsymbol{R}_2^{(\perp\zeta)}$, the set of rotations of π about axes in the $\xi\eta$ plane, with an arbitrary permutation-inversion operation from $\boldsymbol{Q}^*$.

It follows from the considerations above that these operations all leave $H_{\mathrm{int}} + H_{\mathrm{Stark}}$ invariant. We can write the EFS group symbolically as

$$\boldsymbol{G}^{\mathrm{EFS}} = \left\{\boldsymbol{C}_\infty(\text{spatial}) \otimes \boldsymbol{G}^{\mathrm{PSMS}}, \boldsymbol{R}_2^{(\perp\zeta)}\, \boldsymbol{Q}^*\right\}, \tag{14-146}$$

where $\boldsymbol{R}_2^{(\perp\zeta)}\, \boldsymbol{Q}^*$ is the set of operations obtained by combining all operations in $\boldsymbol{R}_2^{(\perp\zeta)}$ with all operations in $\boldsymbol{Q}^*$. The group $\boldsymbol{G}^{\mathrm{EFS}}$ is the appropriate symmetry group for classifying the eigenstates of $\hat{H}_{\mathrm{int}} + \hat{H}_{\mathrm{Stark}}$. Since time reversal symmetry is not spoiled by an electric field, it can give rise to degeneracies that are not predicted by the EFS group symmetry [Chapter 7; see also Watson (1975)].

Unlike the MFS group of Eq. (14-142) the EFS group of Eq. (14-146) is not usually the direct product of two simpler groups. Consequently a comprehensive symmetry analysis of the possible interactions in the presence of an external electric field requires us to construct the complete EFS group, determine its irreducible representations, and classify the relevant eigenstates in it; we cannot do the symmetry classification in separate subgroups of the EFS group as we could for the MFS group in the treatment of the Zeeman effect. Watson (1975), however, has shown that in some cases, the symmetry analysis can be simplified.

The simplest case is encountered for MS groups that contain permutation operations only. For such a group $\boldsymbol{Q}^*$ contains no elements and $\boldsymbol{G}^{\mathrm{PSMS}} = \boldsymbol{G}^{\mathrm{MS}}$. The possible MS groups are $\boldsymbol{C}_n(\mathrm{M})$, $\boldsymbol{D}_n(\mathrm{M})$, $\boldsymbol{T}(\mathrm{M})$, $\boldsymbol{O}(\mathrm{M})$ and $\boldsymbol{I}(\mathrm{M})$. In this case we have

$$\boldsymbol{G}^{\mathrm{EFS}} = \boldsymbol{C}_\infty(\mathrm{spatial}) \otimes \boldsymbol{G}^{\mathrm{MS}}, \tag{14-147}$$

and we can classify the basis functions separately in $\boldsymbol{C}_\infty$(spatial) and $\boldsymbol{G}^{\mathrm{MS}}$. The irreducible representations of $\boldsymbol{C}_\infty$(spatial) are given in Table 14-2, and the molecular states span the representations Σ, Π, Δ etc., as $m_F = 0, \pm 1, \pm 2$, etc., exactly as in the case of the Zeeman effect. Because of time reversal symmetry, states with $m_F = \pm|m_F|$ are degenerate, and the eigenstates of $\hat{H}_{\mathrm{int}} + \hat{H}_{\mathrm{Stark}}$ can be labeled by their value of $M_F = |m_F|$ and by the MS group label.

Another, relatively simple case occurs for MS groups that can be written as

$$\boldsymbol{G}^{\mathrm{MS}} = \boldsymbol{G}^{\mathrm{PSMS}} \otimes \{E, \boldsymbol{Q}^*\}, \tag{14-148}$$

i.e., as the direct product of their PSMS group with a group of order two containing the identity operation and only one permutation-inversion operation $\boldsymbol{Q}^*$. The molecular symmetry groups included are $\boldsymbol{C}_{\mathrm{i}}(\mathrm{M})$, $\boldsymbol{C}_{\mathrm{s}}(\mathrm{M})$, $\boldsymbol{C}_{2\mathrm{v}}(\mathrm{M})$, $\boldsymbol{C}_{n\mathrm{h}}(\mathrm{M})$, $\boldsymbol{S}_{4n+2}(\mathrm{M})$, $\boldsymbol{D}_{n\mathrm{h}}(\mathrm{M})$, $\boldsymbol{D}_{(2n+1)\mathrm{d}}(\mathrm{M})$, $\boldsymbol{T}_{\mathrm{h}}(\mathrm{M})$, $\boldsymbol{O}_{\mathrm{h}}(\mathrm{M})$ and $\boldsymbol{I}_{\mathrm{h}}(\mathrm{M})$, where n is any integer. For these MS groups, we have

$$\boldsymbol{G}^{\mathrm{EFS}} = \left\{\boldsymbol{C}_\infty(\mathrm{spatial}), \boldsymbol{R}_2^{(\perp C)}\boldsymbol{Q}^*\right\} \otimes \boldsymbol{G}^{\mathrm{PSMS}}. \tag{14-149}$$

The group $\left\{\boldsymbol{C}_\infty(\mathrm{spatial}), \boldsymbol{R}_2^{(\perp C)}\boldsymbol{Q}^*\right\}$ is isomorphic to the point group $\boldsymbol{C}_{\infty\mathrm{v}}$ whose irreducible representations are given in Table A-19. We can classify the molecular states separately in this group and in $\boldsymbol{G}^{\mathrm{PSMS}}$. In the group isomorphic to $\boldsymbol{C}_{\infty\mathrm{v}}$, states with $m_F = 0$ transform according to the irreducible representation Σ^+ or Σ^-, and states with $M_F > 0$ span $\Pi, \Delta, \Phi, \ldots$, as $M_F = 1, 2, 3, \ldots$. Thus we can label the states by their value of M_F [for $m_F = 0$, we distinguish between Σ^+ or Σ^- by using the labels 0^+ and 0^-] and by the PSMS group label.

For the MS groups not included in the two cases just treated, the EFS group cannot be written as a direct product, and the symmetry analysis is more complicated. Watson (1975) gives detailed discussions of three such cases, $\boldsymbol{C}_{3\mathrm{v}}(\mathrm{M})$, $\boldsymbol{D}_{2\mathrm{d}}(\mathrm{M})$ and $\boldsymbol{T}_{\mathrm{d}}(\mathrm{M})$. Symmetry in combined electric and magnetic fields and the inclusion of nuclear spin are also considered by Watson (1975).

The EFS groups of nonrigid molecules have not been discussed or used in the literature. Perhaps the Stark effect in the ammonia dimer might be an example to consider (see Section 16.5.2).

The electric dipole spectrum of a molecule in an electric field will consist of the normal (zero field) electric dipole transitions, and these will be shifted or split by the field. In addition to these transitions it is possible that one might be able to detect weak additional transitions made allowed by interactions caused by H_{Stark}. Since these interactions satisfy electric dipole transition selection rules the additional transitions will be those that constitute allowed two-photon electric dipole transitions of the isolated molecule.

BIBLIOGRAPHICAL NOTES

Optical selection rules and forbidden transitions

Herzberg (1991a). Chapter III discusses the selection rules for the appearance of vibrational transitions, and for the appearance of forbidden transitions, in the infrared and Raman spectra of polyatomic molecules in their ground electronic states. Chapter IV discusses the selection rules on the rotational quantum numbers, and the appearance of forbidden transitions, in rotation-vibration transitions.

Herzberg (1991b). Chapter II discusses the selection rules, and the appearance of forbidden transitions, in electronic transitions.

Watson (1971b). It is shown that some of the pure rotation transitions of polyatomic molecules that are forbidden according to rigid rotor selection rules (i.e., obtained using a completely separable rotation-vibration wavefunction) can acquire intensity as a result of centrifugal distortion. Methane and H_3^+ are two important molecules to which this theory applies.

Dorney and Watson (1972). This is a follow up to Watson (1971b) and deals with Stark effects and $\Delta J = 0$ transitions of $\boldsymbol{T}_d$ molecules.

Oka (1976). In this review article entitled 'Forbidden Rotational Transitions' the results of several experimental studies are presented.

Ortho-para transitions

Raich and Good (1964). In the ground vibronic state of the hydrogen molecule pure rotation ortho-para transitions are strongly forbidden, but not strictly forbidden. For example, the transition from the $F = J = N = 0$ para level to the $F = 1$ component of the $J = N = 1$ ortho level satisfies Eqs. (14-10) and (14-11). In this forbidden transition the lower state has rovibronic symmetry $\Sigma_g{}^+$ (+s), and rovibronic-nuclear spin symmetry $\Sigma_u{}^+$ (+a), whereas the upper state has rovibronic and rovibronic-nuclear spin symmetry $\Sigma_g{}^-$ (−a). The symmetry labels are obtained by using the group $\boldsymbol{D}_{\infty h}$(M) [see Fig. 17-6, and Tables A-18 and A-20]. This transition steals intensity from electronic transitions. For example, in a $^1\Sigma_u{}^+$ excited electronic state the $N = J = 1$ level has rovibronic symmetry $\Sigma_u{}^-$ (−s), and has to be a para ($I = 0$) state with rovibronic-nuclear spin symmetry $\Sigma_u{}^-$ (−a). A transition to this excited state level from the ground state $J = 0$ level is not forbidden as an electric dipole transition, and this excited state level can be mixed by terms in $\hat{H}_{ns}$ (see Table 7-1) with the $J = 1$ level of the ground state. Summing over all excited electronic states that can contribute leads to the conclusion that the probability of the spontaneous $J \rightarrow J-1$ pure rotation transition in the ground vibronic state of the hydrogen molecule is $J^6/[(2I+1)(2J+1)(5 \times 10^{11})]$ year^{-1}, where I is the initial nuclear spin. The calculation assumes a mean electronic excitation energy of 12 eV for the states that give the intensity, and it is estimated that this approximation leads to an uncertainty of about 20% in the result. The radiative lifetime of the $J = 1$ level of the H_2 molecule is thus about 5×10^{12} years, which is two orders of magnitude greater than the age of the universe ($\approx 10^{10}$ years). This value for the radiative lifetime leads to the value 10^{-10} D for the electric dipole transition moment for the ortho-para $J = 1 \leftarrow 0$ transition in the ground vibronic state of the hydrogen molecule. The effect of electronic g/u mixing in H_2^+ is discussed in Section 17.7, and this is simultaneously ortho-para interaction; it provides intensity for ortho-para transitions in H_2^+ and these have not yet been observed.

Ozier, Yi, Khosla and Ramsey (1970). The first report of the observation of forbidden ortho-para transitions. The transitions are observed in the $J = 2$ state of the ground vibronic state of methane by combining a level-crossing technique with conventional molecular beam magnetic resonance. The ortho-para interaction involved is enhanced by using a magnetic field to bring the pair of interacting levels close together in energy. These results are analyzed by Hougen (1971) using the MS group $\boldsymbol{T}_d$(M) [see Table A-14] and the CNPI group $\boldsymbol{G}_{48}$ [see Table A-29]. The fact that elements of an MS group do not invert molecule fixed axes is pointed out explicitly by Hougen. In the presence of a magnetic field levels can interact with each other only if they have the same symmetry in the CNPI group and the same value of m_F [see Section 14.4]. Hougen shows that the experimental results do demonstrate ortho-para interactions and transitions, but that they cannot give information on the inversion splitting in methane.

Bordé, Bordé, Salomon, Van Lerberghe, Ouhayoun, and Cantrell (1980). A report of the observation of ortho-para interactions and transitions in the SF_6 molecule. These results could be analyzed using the MS group $\boldsymbol{O}_h(M)$ [see Table A-15] and the group $\boldsymbol{K}$(spatial).

Overtone spectroscopy, highly excited vibrational states and IVR

Chemical Physics (1995). This is a special issue on overtone spectroscopy and dynamics and the following two papers are from it.

Utz, Carrasquillo, Tobiason, and Crim (1995). This is an experimental study of $\Delta v = 3$ transitions of the CH stretching modes in HCCH.

Gambogi, Pearson, Yang, Lehmann, and Scoles (1995). This is an experimental study of CH overtone bands in diacetylene and diacetylene-d_1.

Lubich, Boyarkin, Settle, Perry, and Rizzo (1995). Intensity stealing in highly excited vibrational states of CH_3OH are studied.

Herman, El Idrissi, Pisarchik, Campargue, Gaillot, Biennier, Di Lonardo, and Fusina (1998). Overtone spectroscopy for C_2D_2 is discussed.

Cavagnat and Lespade (1997). Overtone spectroscopy of CH_3NO_2. See Section 15.4.2 on page 511.

Ye, Ma, and Hall (1998). The operating principles and performance levels for several methods of achieving high sensitivity in spectral absorption measurements are reviewed. An extraordinary sensitivity of 5×10^{-13} is achieved using noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE OHMS), and measurement of a saturated absorption signal at about 1064 nm for the R(6) line of the $(v_1, v_2, v_3) = (2,0,3) \leftarrow (0,0,0)$ band in $^{12}C^{16}O_2$ is made; this has an electric dipole transition moment of about 6×10^{-6} D.

Neuhauser, Braun, Neusser and van der Avoird (1998). High overtones of the benzene-argon intermoiety vibration have been studied using coherent ion dip spectroscopy (CIS). This is an alternative method of accessing highly excited vibrational states.

Ishikawa, Chen, Ohshima, Wang and Field (1996). Stimulated emission pumping (SEP) spectroscopy is used to access the $(v_1, v_2, v_3) = (0,26,0)$ to $(0,42,0)$ bending overtone levels of HCP; the highest of these levels is at an energy of over 25000 cm^{-1} above the (0,0,0) level. This technique involves pumping molecules from the ground ($\tilde{X}$) state into levels of an excited electronic state that is not subject to significant predissociation (for HCP this is the $\tilde{A}$ or $\tilde{C}$ excited state) using a pulsed 'pump' laser, and then stimulating emission using a pulsed 'dump' laser into high overtone levels of the ground electronic state. In assigning such highly excited states it is very important, and useful, to categorize the various polyad structures that occur, and to use polyad quantum numbers.

Dai and Field (1995). This book, entitled "Molecular Dynamics and Spectroscopy by Stimulated Emission Pumping," has several articles on IVR.

Nesbitt and Field (1996). This is a pedagogical review of IVR, and the interplay of theory and experiment is stressed.

Zeeman and Stark effects

Bowater, Brown, and Carrington (1973). The general theory is presented for the description of the rotational energy levels of a nonlinear open-shell molecule in the presence of an external electric or magnetic field. The selection rules are determined and expressions for the relative intensities of the lines in the microwave spectrum are derived. Irreducible tensor methods are used throughout. For the HCO free radical in a weak magnetic field (up to 200 mT) the microwave spectrum between 8.3 and 8.7 GHz is obtained and analyzed.

Shostak, Ebenstein, and Muenter (1991). An example of experimental measurements of Stark splittings (for H_2O) is given.

Mengel and Jensen (1995). A calculation of the Stark splittings for H_2O is made directly from the dipole moment surface. The Schrödinger equation for $\hat{H} = \hat{H}_{\text{int}} + \hat{H}_{\text{Stark}}$ is solved by first or second order perturbation theory, considering $\hat{H}_{\text{Stark}}$ as a perturbation. The dipole moment surface is refined in a least squares fitting to experimental Stark data for H_2O.

15

Nonrigid Molecules

Nonrigid molecules have one or more large amplitude internal coordinates in the electronic state (or states) under investigation, and to understand their symmetry and spectroscopy we begin with the derivation of an appropriate zero order rotation-vibration Hamiltonian. The approach used for a rigid molecule in Chapters 10 and 11, must be modified. The zero order Hamiltonian for a nonrigid molecule is set up as discussed by Hougen, Bunker and Johns (1970) [called HBJ], and perturbation theory is used to allow for the neglected terms arising from the effects of the small amplitude vibrations. The zero order wavefunctions are symmetry classified in the MS group. The selection rules for electric dipole transitions in nonrigid molecules have to be re-examined, particularly as far as the vibrational and electronic degrees of freedom are concerned. We consider several molecules (ammonia, nitromethane, toluene, ethane, dimethylacetylene, hydrogen peroxide, ethylene and methylene) in order to illustrate a variety of problems that can occur in the symmetry and spectroscopy of nonrigid molecules. For example, for nonrigid molecules having identical coaxial internal rotors (such as hydrogen peroxide, ethylene, ethane and dimethylacetylene) it is not possible to classify the vibronic eigenfunctions, and the other separate basis wavefunctions, in the MS group, but rather it is necessary to introduce and use the extended molecular symmetry (EMS) group. We also discuss the unusual rotational energy level clustering caused by centrifugal distortion in highly excited rotational states; this type of nonrigidity is exemplified here by the H_2Te molecule. Weakly bound cluster molecules are a special type of nonrigid molecule and for them the rotation-vibration Hamiltonian, and the derivation of the electric dipole selection rules, are discussed in Chapter 16.

15.1 INTRODUCTION

We are concerned here with understanding the symmetry and spectroscopy of molecules for which it is necessary to allow for large amplitude internal coordinate changes. 'Large amplitude' in this context means a distortion that is of the order of the length of a bond or the value of a bond angle, and it almost always involves the nuclei tunneling through barriers that separate accessible minima in the potential energy surface V_N of the electronic state under investigation. As a first step in trying to understand the spectrum of such a molecule we set up the MS group to symmetry label the energy levels, and this is explained in Chapter 3. To label the molecular energy levels using the irreducible representations of the MS group we must choose molecular coordinates that lead to an appropriate zero order Hamiltonian and diagonalize the matrix representation of the Hamiltonian. The classification of the eigenfunctions of the zero order Hamiltonian in the MS group gives the desired symmetry labels. An appropriate zero order Hamiltonian in this context is such that its eigenvalues are close enough to the exact ones that it can be used to assign and symmetry label the exact ones.

To set up an appropriate zero order Hamiltonian for a nonrigid molecule we begin, just as for a rigid molecule, by neglecting spin coupling terms and by making the Born-Oppenheimer approximation. As a result the zero order nuclear spin wavefunctions and the electronic wavefunctions are as for a rigid molecule, and the form of them, and the way they are determined, require no further discussion. The classification of the nuclear spin wavefunctions in the MS group, and the determination of the nuclear spin statistical weights, is discussed for all molecules (rigid and nonrigid) in Chapter 8. The classification of the electronic wavefunctions in the MS group of a nonrigid molecule requires the transformation properties of the electronic coordinates in the MS group to be determined. The zero order rotation-vibration Hamiltonian of a nonrigid molecule is not the same as for a rigid molecule because the Taylor series expansions of both $\mu_{\alpha\beta}$ [see Eq. (10-154)] and V_N [see Eq. (10-143)] in the exact Hamiltonian cannot, in general, be satisfactorily approximated by their leading terms when one or more of the vibrational coordinates is of large amplitude. A special discussion is therefore required of the rotation-vibration Hamiltonian, the rotation-vibration coordinates, and the rotation-vibration wavefunctions of a nonrigid molecule. We will call any large amplitude vibrational coordinate of a nonrigid molecule a *contortional coordinate*, and to emphasize its presence the rotation-vibration Hamiltonian of a nonrigid molecule will be called the rotation-contortion-vibration Hamiltonian.

15.2 THE ROTATION-CONTORTION-VIBRATION WAVE EQUATION

The rotation-contortion-vibration wave equation of a nonrigid molecule can be solved in a way that closely parallels the traditional way of solving the rotation-vibration wave equation of a rigid molecule. This is exemplified by the work of HBJ. It involves using Eckart and Sayvetz conditions (as explained below) to define the rotational and contortional coordinates in order to set up the zero order rotation-contortion-vibration Hamiltonian as the sum of a rotation-contortion Hamiltonian and a vibrational Hamiltonian. Thus, in zero order, we do not separate rotation from vibration but rather we separate rotation-contortion from the ordinary small amplitude vibrations. The use of Eckart and Sayvetz conditions ensures that this separation involves minimum approximation. We solve the rotation-contortion Hamiltonian and then use contact transformation perturbation theory to account for the effects of the ordinary small amplitude vibrations; this leads to an effective rotation-contortion Hamiltonian. For the triatomic molecule, following HBJ, such an effective rotation-bending Hamiltonian has been analytically developed [Hoy and Bunker (1974,1979), Jensen and Bunker (1983), Jensen (1983a), Jensen and Bunker (1986)]. The effective rotation-contortion Hamiltonian can be used in a fitting to data (by varying the parameters in it), or in a straight through calculation of the rotation-contortion energies of a particular small amplitude vibrational state (using *ab initio* or presumed values for the parameters). For very small nonrigid molecules it is possible to use the variational approach as discussed in Chapter 13 to calculate numerically the rotation-contortion-vibration energy levels and wavefunctions. As explained in Chapter 13 the variational approach starts out using the exact rotation-vibration Hamiltonian, and we do not discuss it further in this chapter. For the purpose of symmetry labeling the energy levels it is best, if possible, to use wavefunctions obtained from an appropriate zero order separable Hamiltonian that can be readily diagonalized.

15.2.1 The Hamiltonian

To appreciate the approach used in setting up the Hamiltonian for a nonrigid molecule we first summarize the method used for setting up the Hamiltonian of a rigid nonlinear molecule as discussed in Chapters 10 and 11:

(i) We obtain the rotation-vibration Hamiltonian, $H_{\rm rv} = T_{\rm N} + V_{\rm N}$, in the coordinates $(\xi_2, \eta_2, \zeta_2, \zeta_2, \ldots, \xi_N, \eta_N, \zeta_N)$ for the electronic state of interest after having made the Born-Oppenheimer approximation. The (ξ, η, ζ) axis system has origin at the nuclear center of mass and is oriented parallel to the space fixed axis system.

(ii) We change the coordinates in $H_{\rm rv}$ to $(\theta, \phi, \chi, Q_1, \ldots, Q_{3N-6})$, where the expressions for the Euler angles (θ, ϕ, χ) in terms of the (ξ_i, η_i, ζ_i) coordinates are obtained from the Eckart equations, and the expressions for the normal coordinates Q_r in terms of the (ξ_i, η_i, ζ_i) coordinates are obtained by using the *l* matrix. The Euler angles define the orientation of the molecule fixed (x, y, z) axes relative to the (ξ, η, ζ) axes. This might seem a strange thing to say but some people get confused about the molecule fixed (x, y, z) axes: The axes are ***always*** right handed and their orientation in space is given by the Euler angles. We use the Podolsky trick to transform $H_{\rm rv}$ to the quantum mechanical operator $\hat{H}_{\rm rv}$ which is expressed in terms of the components of the rovibronic angular momentum operator $\hat{J}_\alpha$ ($\alpha = x, y$, or z), the normal coordinates Q_r, and their conjugate momenta $\hat{P}_r$ ($r = 1$ to $3N-6$). The kinetic energy operator $\hat{T}_{\rm N}$ involves the elements $\mu_{\alpha\beta}$ of the 3×3 matrix $\boldsymbol{\mu}$, and it is given in Eq. (10-150). The potential energy expression $V_{\rm N}$ is given in Eq. (10-143).

(iii) We expand $\mu_{\alpha\beta}$ and $V_{\rm N}$ as Taylor series, about their values at equilibrium, in the normal coordinates Q_r [see Eqs. (10-154) and (10-143)].

(iv) The zero order rotation-vibration Hamiltonian H^0_{rv} is obtained by neglecting all but the leading terms ($\mu^{\mathrm{e}}_{\alpha\beta}$ and $\frac{1}{2}\sum\lambda_r Q_r{}^2$) in the Taylor series expansions of $\mu_{\alpha\beta}$ and V_{N}, and by neglecting the vibrational angular momenta p_α and electronic angular momenta L_α. The Hamiltonian H^0_{rv} obtained is the sum of a three-dimensional rigid rotor Hamiltonian and of $3N-6$ one-dimensional harmonic oscillator Hamiltonians [see Eq. (10-155)]. Using the Eckart conditions the p_α are minimized so that their neglect is not usually a bad approximation, and the l matrix is such that the leading term in V_{N} contains no cross terms $\Phi_{rs}Q_rQ_s$ to prevent the zero order separation of the $3N-6$ harmonic oscillators. The eigenfunctions of this Hamiltonian are functions of the Euler angles and normal coordinates (see Chapter 11), and they can be classified in the MS group once the transformation properties of the coordinates have been determined (see Chapter 12).

(v) Contact transformation perturbation theory is used to account for the neglected Coriolis coupling terms involving the vibrational angular momenta p_α, and the neglected terms from the Taylor series expansions of $\mu_{\alpha\beta}$ and V_{N}, and the resulting Hamiltonian is averaged over the vibrational state [see Section 13.2.4]. As a result an effective rotational Hamiltonian (the Watsonian) is obtained. The Watsonian is a sum of quadratic, quartic, sextic, etc., terms in the angular momentum operators J_x, J_y and J_z.

The approach used to obtain the zero order rotation-contortion-vibration Hamiltonian of a nonrigid molecule is slightly different [see, for example, the review by Sørensen (1979)]. This is because in this case we cannot usually approximate both $\mu_{\alpha\beta}$ and V_{N} by their leading terms in a Taylor series expansion about equilibrium; the contortional coordinate is of large amplitude and can prevent the convergence of either or both of the series (using rigid molecule formalism the lack of convergence of $\mu_{\alpha\beta}$ and V_{N} would give rise to a large centrifugal rotation-contortion interaction and a large anharmonic contortion-vibration interaction, respectively). The approach used for a molecule with one contortional coordinate is as follows:

(i) We obtain the rotation-contortion-vibration Hamiltonian H_{rcv} ($= T_{\mathrm{N}} + V_{\mathrm{N}}$) in the coordinates ($\xi_2$, η_2, ζ_2, $\ldots$,ξ_N, η_N, ζ_N) after having made the Born-Oppenheimer approximation; this Hamiltonian will be basically the same whether or not the molecule in the electronic state under consideration is rigid or nonrigid.

(ii) We change coordinates in H_{rcv} to $(\theta, \phi, \chi, \rho, Q_1, \cdots, Q_{3N-7})$, where ρ is the contortional coordinate. The expressions for the Euler angles (θ, ϕ, χ) in terms of the (ξ_i, η_i, ζ_i) coordinates are obtained from the Eckart equations, the expression for ρ in terms of the (ξ_i, η_i, ζ_i) coordinates is obtained from a *Sayvetz* equation [Sayvetz (1939), see Eq. (15-20) below], and the expressions for the $3N-7$ normal coordinates Q_r are obtained from the l matrix. The elements of the l matrix will depend on ρ. Once again the (x, y, z) axes are ***always*** right handed and their orientation in space is determined by the Euler angles. We use the Podolsky trick to transform H_{rcv} to the quantum mechanical operator H_{rcv} which is expressed in terms of the components of the rovibronic angular momentum operator J_α ($\alpha = x, y$ or z), the contortional coordinate ρ, the contortional momentum operator $J_\rho = -i\hbar\partial/\partial\rho$, the normal coordinates Q_r and their conjugate momenta P_r. As shown by HBJ [see also Eq. (1) of Sarka and Bunker (1987)] the kinetic energy operator in this Hamiltonian can be made to look similar to $\hat{H}_{\mathrm{rv}}$ for a rigid molecule [see Eqs. (10-150)] except that the sum over x, y and z becomes a sum over x, y, z and ρ (and the μ matrix becomes a 4×4 matrix), and the sum over r runs from 1 to $3N-7$, rather than from 1 to $3N-6$, since we have removed the contortional coordinate (ρ) from the vibrational problem.

(iii) We expand $\mu_{\alpha\beta}$ (where α and $\beta = x, y, z$ and ρ), and V_{N} about their values when all $3N-7$ Q_r are zero as a Taylor series in the $3N-7$ Q_r with coefficients that depend on ρ. When all $3N-7$ Q_r are zero the molecule is said to be in its *reference* configuration; in the reference configuration the Euler angles and the contortional coordinate are arbitrary. The expansions of $\mu_{\alpha\beta}$ and V_{N} can be written as

$$\mu_{\alpha\beta} = \mu^{\mathrm{ref}}_{\alpha\beta} - \mu^{\mathrm{ref}}_{\alpha\gamma} a_r^{\gamma\delta} \mu^{\mathrm{ref}}_{\delta\beta} Q_r + \cdots \tag{15-1}$$

and

$$V_{\mathrm{N}} = V_0(\rho) + \sum_r \Phi_r Q_r + \frac{1}{2}\sum_r \lambda_r {Q_r}^2 + \frac{1}{6}\sum_{r,s,t} \Phi_{rst} Q_r Q_s Q_t + \cdots, \tag{15-2}$$

where $\alpha, \beta, \gamma, \delta = x, y, z$ or ρ, and $r, s, t = 1, 2, \ldots, 3N-7$; $\mu^{\mathrm{ref}}_{\alpha\beta}$ and the $a_r^{\gamma\delta}$ are functions of ρ, $V_0(\rho)$ is the pure contortional potential function of the reference configuration, and λ_r and the Φ are also functions of ρ. The term linear in Q_r (i.e., $\sum_r \Phi_r Q_r$) occurs in V_{N} because Φ_r is a function of ρ; in the standard (rigid molecule) expansion this term would become (expanding only to quartic terms)

$$\sum_r \left[\Phi_{r\rho}\rho + \frac{1}{2}\Phi_{r\rho\rho}\rho^2 + \frac{1}{6}\Phi_{r\rho\rho\rho}\rho^3\right] Q_r. \tag{15-3}$$

(iv) The zero order rotation-contortion-vibration Hamiltonian $\hat{H}^0_{\mathrm{rcv}}$ is obtained by neglecting all but the leading terms [$\mu^{\mathrm{ref}}_{\alpha\beta}$ and $V_0(\rho) + \frac{1}{2}\sum \lambda_r {Q_r}^2$] in the Taylor series expansions, and by neglecting the vibrational angular and contortional momenta p_α, and electronic angular momenta, that occur in it. The Hamiltonian $\hat{H}^0_{\mathrm{rcv}}$ is the sum of a four-dimensional rotation-contortion Hamiltonian H_{rc} and of $3N-7$ harmonic oscillator Hamiltonians. For a molecule with n contortional coordinates the rotation-contortion Hamiltonian will involve a $(3+n)\times(3+n)$ $\mu_{\alpha\beta}$ matrix, and the vibrational Hamiltonian will be the sum of $3N-6-n$ harmonic oscillator Hamiltonians; the $\mu^{\mathrm{ref}}_{\alpha\beta}$, $a_r^{\gamma\delta}$, V_0, λ_r and Φ will be functions of all n contortional coordinates.

(v) Contact transformation perturbation theory is used to account for the neglected Coriolis coupling terms involving the vibrational angular and contortional momenta p_α, and the neglected terms from the Taylor series expansions of $\mu_{\alpha\beta}$ and V_N. As a result an effective rotation-contortion Hamiltonian is obtained. This is a sum of quadratic, quartic, sextic, etc., terms in the momentum operators $\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$, and $\hat{J}_\rho$ and it also includes the effective contortional potential function. The effective contortional potential function will be isotope dependent, and it will depend on the small amplitude vibrational state.

We begin by studying the rotation-contortion Hamiltonian and the vibrational Hamiltonian that together make up the zero order rotation-contortion-vibration Hamiltonian. The rotation-contortion Hamiltonian for a molecule with one contortional coordinate is given by [see Eq. (33) of HBJ and Eq. (9) of Sarka (1971)]

$$\hat{H}_{rc} = \frac{1}{2}\mu^{1/4}\sum_{\alpha,\beta}\hat{J}_\alpha\mu^{-1/2}\mu^{\text{ref}}_{\alpha\beta}\hat{J}_\beta\mu^{1/4} + V_0(\rho), \tag{15-4}$$

where α, $\beta = x, y, z$ or ρ, and μ is the determinant of the 4×4 matrix $\boldsymbol{\mu}^{\text{ref}}$ having elements $\mu^{\text{ref}}_{\alpha\beta}$. The quantities $\mu^{\text{ref}}_{\alpha\beta}$ and $V_0(\rho)$ all depend on ρ in the general case. This means that μ and the $\mu^{\text{ref}}_{\alpha\beta}$ do not commute with $\hat{J}_\rho$ and we cannot remove the determinant μ from $\hat{H}_{rc}$. Using the commutation relation given in Eq. (13) of Hougen (1965) $\hat{H}_{rc}$ can be simplified to

$$\hat{H}_{rc} = \frac{1}{2}\sum_{\alpha,\beta}\mu^{\text{ref}}_{\alpha\beta}\hat{J}_\alpha\hat{J}_\beta + \frac{1}{2}\sum_{\beta}(\hat{J}_\rho\mu^{\text{ref}}_{\rho\beta})\hat{J}_\beta + \frac{1}{2}\mu^{1/4}[\hat{J}_\rho\mu^{-1/2}\mu^{\text{ref}}_{\rho\rho}(\hat{J}_\rho\mu^{1/4})] + V_0(\rho), \tag{15-5}$$

where the [ ] and ( ) brackets indicate, for example, that in the second term $\hat{J}_\rho$ acts only on $\mu^{\text{ref}}_{\rho\beta}$.

For certain molecules a value of ρ is accessible for which one or more of the ρ-dependent functions $\mu^{\text{ref}}_{\alpha\beta}$ become infinite; i.e., become a ***singular*** function of ρ. In this circumstance the determinant μ, and the third term in Eq. (15-5), will also be singular functions of ρ. The diagonalization of a rotation-contortion Hamiltonian containing singular $\mu^{\text{ref}}_{\alpha\beta}$ elements has to be performed in a special way. The most common type of molecule for which this occurs is a so-called ***quasilinear*** molecule, and below we treat the methylene molecule CH_2 in its ground electronic state as an example. Another situation in which singular $\mu^{\text{ref}}_{\alpha\beta}$ could occur would be internally rotating methanol in highly excited COH bending states (a two-contortional coordinate problem) if a structure with a linear COH bond became accessible. We develop the theory for molecules in which the $\mu^{\text{ref}}_{\alpha\beta}$ elements remain finite for all accessible values of ρ, and leave the discussion of how to diagonalize a rotation-contortion Hamiltonian containing singular $\mu^{\text{ref}}_{\alpha\beta}$ elements until we deal with the methylene molecule.

The third term in Eq. (15-5) is called $U_1(\rho)$ and it is often ignored [it obviously cannot be ignored for the molecules discussed in the previous paragraph since for them $U_1(\rho)$ is singular]. It comes from the kinetic energy but it appears as a (small) nuclear-mass-dependent correction to the contortional potential. If one does include $U_1(\rho)$ then one should also include the term $U_0(\rho)$ which is of the same order of magnitude and which arises from the similar vibrational kinetic energy term $\frac{1}{2}\mu^{1/4}\sum_r[\hat{P}_r\mu^{-1/2}(\hat{P}_r\mu^{1/4})]$, where in this expression μ is the determinant of the matrix having Q_r dependent elements $\mu_{\alpha\beta}$ given in Eq. (15-1). We write

$$U(\rho) = U_0(\rho) + U_1(\rho), \tag{15-6}$$

and it can be shown that

$$U(\rho) = -\frac{\hbar^2}{8}\left[\mu^{\text{ref}}_{xx} + \mu^{\text{ref}}_{yy} + \mu^{\text{ref}}_{zz} + \mu^{\text{ref}}_{\rho\rho}c(\rho)\right] \tag{15-7}$$

where $c(\rho)$ is an analytic function of the masses and bond lengths in the reference configuration [see Sarka and Bunker (1987)]. $U(\rho)$ is the nonrigid molecule analog of the rigid molecule term U given in Eq. (10-153). If all the elements of $\mu^{\text{ref}}_{\alpha\beta}$ are independent of ρ, and therefore commute with $\hat{J}_\rho$, then the second and third terms in the expression for $\hat{H}_{\text{rc}}$ in Eq. (15-5) will completely disappear. This fortunate state of affairs occurs for the nitromethane molecule, which we discuss as an example below.

The rotation-contortion-vibration Hamiltonian of a nonrigid molecule is presented here in a way that makes it look very similar to the rotation-vibration Hamiltonian of a rigid molecule (see Section 10.5). This is deceptive. Because the $\mu^{\text{ref}}_{\alpha\beta}$, $a_r^{\gamma\delta}$, λ_r and Φ are functions of the contortional coordinate many complications arise. One obvious result is that the $\mu^{\text{ref}}_{\alpha\beta}$ do not commute with $\hat{J}_\rho$. This means that[1]

$$\frac{1}{2}\sum_\beta(\hat{J}_\rho\mu^{\text{ref}}_{\rho\beta}\hat{J}_\beta + \hat{J}_\beta\mu^{\text{ref}}_{\beta\rho}\hat{J}_\rho) \neq \sum_\beta \mu^{\text{ref}}_{\rho\beta}\hat{J}_\rho\hat{J}_\beta \tag{15-8}$$

for $\beta \neq \rho$,

$$\frac{1}{2}\hat{J}_\rho\mu^{\text{ref}}_{\rho\rho}\hat{J}_\rho \neq \frac{1}{2}\mu^{\text{ref}}_{\rho\rho}\hat{J}^2_\rho, \tag{15-9}$$

and in $\hat{H}_{\text{rc}}$ [see Eq. (15-5)] the term $\frac{1}{2}\sum_\beta(\hat{J}_\rho\mu^{\text{ref}}_{\rho\beta})\hat{J}_\beta$ occurs. If we were to omit this term then $\hat{H}_{\text{rc}}$ would not be Hermitian. The operators on the left hand sides of Eqs. (15-8) and (15-9) are Hermitian but those on the right hand sides are not if $\mu^{\text{ref}}_{\rho\beta}$ depends on ρ. In the effective Hamiltonian $\hat{H}^{\text{eff}}_{\text{rc}}$ discussed below [see Eq. (15-16)] the term $\tau_{\alpha\beta\gamma\delta}\hat{J}_\alpha\hat{J}_\beta\hat{J}_\gamma\hat{J}_\delta$ is generally not Hermitian if $\tau_{\alpha\beta\gamma\delta}$ depends on ρ and one has to include terms such as $(\hat{J}_\rho\tau_{\rho\beta\gamma\delta})\hat{J}_\beta\hat{J}_\gamma\hat{J}_\delta$. Such terms usually are of small magnitude unless there are singularities.

The 4×4 matrix $\boldsymbol{\mu}^{\text{ref}}$ is the inverse of the 4×4 generalized moment of inertia matrix $\boldsymbol{I}^{\text{ref}}$ of the reference configuration. The elements of $\boldsymbol{I}^{\text{ref}}$ are given by:

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[1] $\mu^{\text{ref}}_{\rho\beta} = \mu^{\text{ref}}_{\beta\rho}$.

$$I^{\rm ref}_{\alpha\alpha} = \sum_i m_i(a^2_{i\beta} + a^2_{i\gamma}), \tag{15-10}$$

$$I^{\rm ref}_{\alpha\beta} = -\sum_i m_i a_{i\alpha} a_{i\beta} \quad \text{with } \alpha \neq \beta, \tag{15-11}$$

$$I^{\rm ref}_{\rho\rho} = \sum_i m_i({a'_{ix}}^2 + {a'_{iy}}^2 + {a'_{iz}}^2), \tag{15-12}$$

and

$$I^{\rm ref}_{\alpha\rho} = -\sum_i m_i(a_{i\gamma} a'_{i\beta} - a_{i\beta} a'_{i\gamma}), \tag{15-13}$$

where m_i is the mass of the ith nucleus, $a_{i\alpha}$ is the Cartesian coordinate of the ith nucleus along the α molecule fixed axis in the reference configuration, $a'_{i\alpha}$ is the partial derivative of this coordinate[2] with respect to ρ, and $[\alpha\beta\gamma]$ must be chosen in cyclic order from $[xyz]$. Note that in Eqs. (15-10) to (15-13) the indices α, β and γ only run over x, y and z.

The orientation of the molecule fixed axes in the reference configuration is normally chosen so that they are the principal inertial axes (in the same way as they are located in the equilibrium configuration of a rigid molecule), and the xy, yz and zx elements of $\mathbf{I}^{\rm ref}$ will then vanish. In the general case using principal axes, however, the $x\rho$, $y\rho$ and $z\rho$ elements of $\mathbf{I}^{\rm ref}$ will not vanish, and after inverting $\mathbf{I}^{\rm ref}$ to obtain $\boldsymbol{\mu}^{\rm ref}$ the Hamiltonian $\hat{H}_{\rm rc}$ that is derived will contain every possible cross term $\hat{J}_\alpha \hat{J}_\beta$ (where α and $\beta = x$, y, z and ρ). For symmetrical molecules like ammonia with inversion, and triatomic ABA molecules having large amplitude bending, it conveniently happens that the $\hat{H}_{\rm rc}$ obtained in this way has no cross terms $\hat{J}_\alpha \hat{J}_\beta$. In HBJ it is shown that for unsymmetrical triatomic molecules having large amplitude bending ρ the axes can be oriented in the reference configuration in an appropriate ρ dependent way so that the only nonvanishing cross term is the $\hat{J}_y \hat{J}_z$ term. This will be discussed further in the CH$_2$ example below. For other nonrigid molecules a choice similar to that made in HBJ for locating the axes in the reference configuration can be made in order to eliminate $\hat{J}_\alpha \hat{J}_\rho$ cross terms in $\hat{H}_{\rm rc}$ [see, for example, Kręglewski (1978) in his treatment of methylamine]. For a molecule with internal rotation the use of principal inertial axes when setting up $\hat{H}_{\rm rc}$ is called *the principal axis method* (PAM). PAM is conceptually simple from the point of view of understanding the Hamiltonian and its symmetry, for determining the transformation properties of the molecular coordinates, and for setting up and using zero-order rotation and internal-rotation basis functions. For example, the internal rotation wavefunctions are periodic in 2π and basis functions like those given in Eq. (15-49) below for the PAM Hamiltonian of nitromethane can be used. For molecules like methanol and acetaldehyde in which there is internal rotation of a methyl group against an asymmetric frame the PAM Hamiltonian does however suffer from the problem, as stated above for the general nonrigid molecule, that it contains nonvanishing rotational cross terms $\hat{J}_x\hat{J}_y$, $\hat{J}_y\hat{J}_z$ and $\hat{J}_z\hat{J}_x$, and nonvanishing Coriolis coupling cross terms $\hat{J}_x\hat{J}_\rho$, $\hat{J}_y\hat{J}_\rho$ and $\hat{J}_z\hat{J}_\rho$. In this case it is customary to 'rotate' the xyz axes (this rotation of axes is achieved by an appropriate contact transformation of the PAM Hamiltonian) to eliminate some of the cross terms in $\hat{H}_{rc}$ before solving the rotation internal-rotation wave equation. There are three degrees of freedom in such a rotation transformation and so in the general case we cannot eliminate all the cross terms, but we can eliminate some of them. If we transform the Hamiltonian so that the $\hat{J}_x\hat{J}_\rho$ and $\hat{J}_y\hat{J}_\rho$ terms are eliminated then the rotation internal-rotation coupling term that remains [the $\hat{J}_z\hat{J}_\rho$ term] will be diagonal in the rotational quantum number K, and this is a convenience in calculations. This is called *the rho axis method* (RAM). It is possible to transform the Hamiltonian so that it contains no $\hat{J}_\alpha\hat{J}_\rho$ cross terms, and this is called *the internal axis method* (IAM); this is analogous to the HBJ axis choice that is made for a triatomic molecule with large amplitude bending. In IAM there is no internal-rotation angular momentum in the xyz axis system and this minimizes rotation internal-rotation interaction; the ρ dependence of the nonvanishing $\mu^{\mathrm{ref}}_{\alpha\beta}$ prevents the complete separation of rotation from internal-rotation. The drawback of the RAM and IAM Hamiltonians is that the momenta and coordinates that occur in them are not simple to understand as they are in the PAM Hamiltonian. The IAM Hamiltonian is worse than the RAM Hamiltonian in this regard. In PAM the Hamiltonian involves the principal axis components of the rovibronic angular momentum, and its eigenfunctions involve the Euler angles that give the orientation of the principal inertial axes of the reference configuration. In RAM and IAM the '$\hat{J}_\alpha$' that occur are a mixture of the $\hat{J}_\alpha$ occurring in the PAM Hamiltonian. The classic review paper by Lin and Swalen (1959) discusses PAM and IAM, and the more recent paper by Hougen, Kleiner and Godefroid (1994) discusses RAM as well.

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[2] Once the reference configuration, and the location of the (x, y, z) axes in it, have been defined, the $a_{i\alpha}$ and $a'_{i\alpha}$ are easily determined.

The rotation-contortion Hamiltonian for a molecule with n contortional coordinates will involve $3 + n$ degrees of freedom, and the extended matrix $\boldsymbol{\mu}^{\mathrm{ref}}$ will be a $(3 + n)\times(3 + n)$ matrix. If we label the contortional coordinates ρ_1, $\rho_2, \ldots, \rho_n$ the rotation-contortion Hamiltonian is given by Eq. (15-4) where α and β are summed over x, y, z, ρ_1, $\rho_2, \ldots, \rho_n$. The $(3 + n)\times(3 + n)$ matrix $\boldsymbol{\mu}^{\mathrm{ref}}$ is the inverse of a $(3 + n)\times(3 + n)$ matrix $\boldsymbol{I}^{\mathrm{ref}}$. The elements of $\boldsymbol{I}^{\mathrm{ref}}$ are obtained by a straightforward extension of Eqs. (15-10)-(15-13). Equations (15-10) and (15-11) are the same, and Eqs. (15-12) and (15-13) are generalized to

$$I^{\mathrm{ref}}_{\rho_j\rho_k} = \sum_i m_i \left[\frac{\partial a_{ix}}{\partial \rho_j}\frac{\partial a_{ix}}{\partial \rho_k} + \frac{\partial a_{iy}}{\partial \rho_j}\frac{\partial a_{iy}}{\partial \rho_k} + \frac{\partial a_{iz}}{\partial \rho_j}\frac{\partial a_{iz}}{\partial \rho_k}\right], \qquad (15\text{-}14)$$

and

$$I^{\rm ref}_{\alpha\rho_j} = -\sum_i m_i \left[a_{i\gamma}\frac{\partial a_{i\beta}}{\partial \rho_j} - a_{i\beta}\frac{\partial a_{i\gamma}}{\partial \rho_j} \right], \tag{15-15}$$

where j, $k = 1, 2, \ldots, n$.

From Eq. (15-4) to here we have discussed the rotation-contortion Hamiltonian. To this we must add the vibrational Hamiltonian. In zero order the vibrational Hamiltonian for a molecule having n contortional coordinates is the sum of $3N - 6 - n$ harmonic oscillator Hamiltonians each of which is like that in Eq. (11-7) but each of which is a parametric function of the ρ_i (in the same way as the electronic Hamiltonian of a molecule is a parametric function of the nuclear coordinates in the Born-Oppenheimer approximation) because of the dependence of the λ_r in Eq. (15-2) on the ρ_i [see Eq. (34) of HBJ]. The normal coordinates and harmonic wavenumbers vary with the ρ_i values; this ρ_i dependence can be determined explicitly if the ρ_i dependence of the molecular force field is known. In higher approximation the ρ_i dependence of the anharmonic force constants will also have to be allowed for.

In the development of the zero order rotation-contortion-vibration Hamiltonian the concept of a reference configuration is central, and it is worth explaining it in some detail. The reference configuration of a nonrigid molecule is the analog of the equilibrium configuration of a rigid molecule. A nonrigid molecule is in its reference configuration when all the small amplitude vibrational displacements are set to zero but when the Euler angles and ρ_i coordinates are arbitrary. The extended moment of inertia tensor $I^{\rm ref}$ of the reference configuration has the elements $I^{\rm ref}_{\alpha\beta}$ just discussed [see Eqs. (15-10)-(15-15)]. Thus, for example, in the hydrogen peroxide molecule the reference configuration is that molecular configuration in which the O–H and O–O bond lengths and H–O–O angles are fixed at their equilibrium values but in which the internal-rotation angle and rotational orientation in space are arbitrary. A criterion is used (usually that of them being principal inertial axes) to locate the molecule fixed (x, y, z) axes in the reference configuration, and the energy levels of the molecule in its reference configuration (as it rotates and contorts) are obtained by diagonalizing its rotation-contortion Hamiltonian [see Eq. (15-5)]. Having defined the reference configuration, the method for locating the (right-handed) (x, y, z) axes in the reference configuration, and the contortional coordinates ρ_i of the reference configuration, it is easy to determine the effect of the elements of the MS group on the coordinates θ, ϕ, χ, and ρ_i.

In the reference configuration just discussed the molecule can be said to ***rigidly contort***, i.e., the ordinary small amplitude bond lengths and angles remain fixed at their equilibrium values as the molecule contorts. For a triatomic molecule with large amplitude bending this approach leads to the ***rigid-bender Hamiltonian*** [Bunker and Stone (1972)]. For the purpose of labeling by symmetry the rotation-contortion states of a nonrigid molecule one need consider only the eigenstates of the zero order rotation-contortion Hamiltonian discussed above for a rigidly contorting molecule, and this is quite straightforward. However, to calculate accurately the energies, or to make a precise fitting to experimental data, improvements in the Hamiltonian are required.

An improvement in the model is obtained by allowing the ordinary bond lengths and angles to relax to their optimum values as the molecule contorts, and in this new reference configuration the molecule *semirigidly contorts*; for a triatomic molecule this leads to the *semirigid-bender Hamiltonian* [Bunker and Landsberg (1977)]. This approach has been extended to larger molecules [see, for example, East and Bunker (1997)], and to molecules in degenerate vibrational states [Jensen (1984) and Jensen and Johns (1986)]. The semirigid-bender Hamiltonian corrects for some of the deficiencies of the rigid-bender Hamiltonian. However, we can allow for the neglected terms in the expansions of $\mu_{\alpha\beta}$ and V_N [see Eqs. (15-1) and (15-2)] in a more systematic and complete way by using contact transformation perturbation theory (see Section 13.2.4). This leads, in a triatomic molecule, to the *nonrigid-bender Hamiltonian* [Hoy and Bunker (1974,1979), Jensen and Bunker (1983), Jensen (1983a), Jensen and Bunker (1986)], which is an effective rotation-bending Hamiltonian in which the effective bending potential, and the effective $\mu_{\alpha\beta}$ elements, are different for each stretching vibrational state, and in which centrifugal distortion and Coriolis coupling arising from the ordinary vibrations are also included [see Eqs. (5.24)-(5.29) in Jensen (1983a)]. Such an effective rotation-inversion Hamiltonian has also been introduced for the four-atomic molecule ammonia [Špirko (1983)]. For a nonrigid molecule larger than four-atomic it would involve very extensive algebra to develop analytically the effective rotation-contortion Hamiltonian because of the increased number of ordinary (small amplitude) vibrations involved. However, one can develop the effective rotation-contortion Hamiltonian in a parameterized form, suitable for fitting data, with the inclusion of centrifugal distortion and Coriolis coupling effects from the ordinary vibrations. With some simplifying approximations we can write the effective rotation-contortion Hamiltonian for a molecule having no singular $\mu^{\text{eff}}_{\alpha\beta}$ elements as

$$H^{\text{eff}}_{\text{rc}} = \frac{1}{2}\sum_{\alpha,\beta}\mu^{\text{eff}}_{\alpha\beta}J_\alpha J_\beta + \frac{1}{2}\sum_{\beta}(J_\rho \mu^{\text{eff}}_{\rho\beta})J_\beta + \frac{1}{4}\sum_{\alpha,\beta,\gamma,\delta}\tau_{\alpha\beta\gamma\delta}J_\alpha J_\beta J_\gamma J_\delta + V_{\text{eff}}(\rho), \tag{15-16}$$

where $\alpha, \beta, \gamma, \delta = x, y, z$ or ρ. The coefficient $\tau_{\alpha\beta\gamma\delta}$ is a generalized centrifugal distortion coefficient involving ρ as a subscript as well as x, y and z. Symmetry can be used to determine which $\mu^{\text{eff}}_{\alpha\beta}$ and $\tau_{\alpha\beta\gamma\delta}$ are nonvanishing since each term in $H^{\text{eff}}_{\text{rc}}$ has to be totally symmetric in the MS group. A recent paper that discusses and solves the general problem of constructing an effective rotation-contortion Hamiltonian for a molecule having any number of contortional coordinates, and which gives a good list of references to other work, is by Makarewicz (1996).

When a nonrigid molecule is not in its reference configuration the Eckart and Sayvetz conditions enable one to calculate the rotational and contortional coordinate values, i.e., we can calculate the values of the coordinates θ, ϕ, χ, and ρ (where here we presume there to be only one contortional coordinate) from the values of the $3N-3$ nuclear coordinates (ξ_i, η_i, ζ_i). Having chosen a convention for locating the (x, y, z) axes in the reference configuration, nucleus i will have coordinates a_{ix}, a_{iy}, and a_{iz} in that axis system. The reference configuration coordinates of all the nuclei in a molecule are known, once the reference configuration is defined, in the same way that the equilibrium nuclear coordinates x_i^e, y_i^e, and z_i^e of a rigid molecule are known. The reference configuration coordinates of each nucleus will not be constants (as are the equilibrium configuration coordinates of a rigid molecule) but they will depend on the contortional angle ρ. The Eckart equations become

$$\sum_{i=1}^{N} m_i(a_{ix}y_i - a_{iy}x_i) = 0, \tag{15-17}$$

$$\sum_{i=1}^{N} m_i(a_{iy}z_i - a_{iz}y_i) = 0, \tag{15-18}$$

and

$$\sum_{i=1}^{N} m_i(a_{iz}x_i - a_{ix}z_i) = 0, \tag{15-19}$$

and the Sayvetz condition is

$$\sum_{\alpha,i} m_i(\alpha_i - a_{i\alpha})a'_{i\alpha} = 0, \tag{15-20}$$

where $\alpha = x, y,$ or z. The $a_{i\alpha}$ and $a'_{i\alpha}$ $(= \partial a_{i\alpha}/\partial\rho)$ are known functions of ρ, and the instantaneous molecule fixed coordinates α_i can be expressed in terms of the direction cosine elements (i.e., the Euler angles) and the known (ξ_i, η_i, ζ_i) nuclear coordinates as done in Eqs. (10-34)-(10-36). We will then have four equations in the four unknowns θ, ϕ, χ, and ρ which can be solved simultaneously for any given set of (ξ_i, η_i, ζ_i) coordinates, i.e., for any given nuclear configuration in space.[3] We also obtain the (x_i, y_i, z_i) coordinates of the nuclei once we know the Euler angles. These equations could be used to determine how θ, ϕ, χ, and ρ are transformed by elements of the MS group but it is easier to study the transformation properties of the reference configuration for this purpose [i.e., we determine the transformation properties of the coordinates θ, ϕ, χ, and ρ when all $3N-7$ Q_r's are zero]. In the same way that the Eckart conditions define "rotation" so as to minimize the terms that couple rotation and vibration in the kinetic energy, the Sayvetz condition defines "contortion" so as to minimize the term that couples contortion and vibration in the kinetic energy. Loosely speaking Eq. (15-20) defines ρ so that the change in nuclear coordinates when ρ is changed, $\partial\alpha_i/\partial\rho$, is orthogonal to the change in nuclear coordinates, $\alpha_i - a_{i\alpha}$, that results from the vibrations. For a molecule with several contortional coordinates there is one Sayvetz condition for each contortional coordinate ρ_j:

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[3] See Fig. 2 and Eq. (8) of HBJ.

$$\sum_{\alpha,i} m_i(\alpha_i - a_{i\alpha})\frac{\partial a_{i\alpha}}{\partial \rho_j} = 0, \qquad (15\text{-}21)$$

where $j = 1, 2, \ldots n$.

15.2.2 The symmetry labeling of states

The rotation-contortion wavefunctions are obtained by diagonalizing a matrix representation of $\hat{H}_{\rm rc}$ in basis functions that are products of the rotational basis functions $\Phi_{\rm rot}(\theta\phi\chi)$, invariably symmetric top functions, and eigenfunctions $\Phi_{\rm con}(\rho)$ of $\hat{H}_{\rm con}$, where

$$\hat{H}_{\rm con} = \frac{1}{2}\mu_{\rho\rho}^{\rm ref}\hat{J}_\rho^2 + \frac{1}{2}(\hat{J}_\rho\mu_{\rho\rho}^{\rm ref})\hat{J}_\rho + U(\rho) + V_0(\rho). \qquad (15\text{-}22)$$

The symmetry classification of the rotation-contortion energy levels is made by classifying the basis functions $\Phi_{\rm rot}(\theta\phi\chi)$ and $\Phi_{\rm con}(\rho)$ in the MS group. Knowing the equivalent rotations of the elements of the MS group makes classifying the $\Phi_{\rm rot}(\theta\phi\chi)$ easy, and the classification of the $\Phi_{\rm con}(\rho)$ follows once the transformation properties of ρ are determined. Normally one determines the contortional species at the high barrier and zero barrier limits. The examples below will show how this is done in practice. The extension of these ideas to a situation in which there is more than one contortional coordinate is, in principle, straightforward and some references are given in the Bibliographical Notes.

In studying rotation-contortion energy levels it is very helpful to construct a correlation diagram connecting the rotation-contortion energy levels of the limiting situations of an high (insuperable) barrier (when there is no tunneling) and of a zero barrier (when the contortional wavefunction is simple to determine and to symmetry classify). The determination of the nonrigid molecule MS group symmetry labels at the high barrier limit proceeds by using the reverse correlation table of the species of the conformer MS group and the nonrigid molecule MS group. The correlation of the high barrier and zero barrier levels is drawn maintaining the MS group symmetry labels and the label J from the group $\boldsymbol{K}$(spatial). As shown at the end of Chapter 8 one can add nuclear spin statistical weights to such correlation tables, and these are helpful in understanding the intensity alternations in the spectrum. Similar correlation diagrams for the contortional levels alone can also be useful, as we show below for the torsional energy levels of the hydrogen peroxide molecule in Fig. 15-13.

The symmetry classification of the vibrational wavefunctions is complicated by the fact that the λ_r are ρ-dependent, and this makes the determination of the symmetry species of the normal coordinates, and hence of the vibrational wavefunctions, more involved than for a rigid molecule. As we allow the contortional coordinate to vary over its allowed range the point group symmetry of the instantaneous nuclear configuration will usually change, e.g., as the dimethylacetylene molecule twists the instantaneous point group symmetry changes from $\boldsymbol{D}_{3h}$ through $\boldsymbol{D}_3$ to $\boldsymbol{D}_{3d}$. For each different point group geometry we can determine the symmetry species, in that point group, of the normal coordinates using the technique discussed in Chapter 12 [see Eq. (12-7)]. Excluding the species of the contortional coordinate from these we obtain the species of the $3N - 7$ normal coordinates in each possible instantaneous point group. We use the correlation tables of these point groups (or really of the rigid molecule MS group with which they are isomorphic) to the nonrigid molecule MS group to determine the species of the normal coordinates in the nonrigid molecule MS group (see the nitromethane example below). The species of the normal coordinates in the nonrigid molecule MS group is often not unique; the species will depend on the details of the ρ dependence of the force field. This means that one begins a spectral simulation by choosing a zero order ρ dependence in the force field, which then leads to zero order normal coordinates. One can then determine zero order rotation-contortion-vibration energy levels, wavefunctions, symmetries, selection rules, intensities and spectra. Neglected terms in the force field could then be introduced in order to determine their effect.

The classification of an electronic wavefunction of a nonrigid molecule in its MS group proceeds after first determining how the electronic coordinates transform. The toluene and ethylene molecules treated below as examples will show how this is done. If more than one electronic state is considered in a problem then one will need to use the MS group that is appropriate for the simultaneous treatment of the states (see Section 3.5).

15.3 OPTICAL SELECTION RULES

The rigorous electric dipole selection rules obtained in Eqs. (14-8)-(14-11) apply to all molecules, rigid, nonrigid, and linear. The general line strength expressions in Eqs. (14-33), (14-43), (14-48), and (14-50) are also valid for all molecules [where the $\Phi_{\mathrm{vib}}^{(V,L)}$ in Eq. (14-44) include Φ_{con}] and so are, consequently, all near selection rules on angular momentum quantum numbers that can be derived from these equations, such as Eqs. (14-30), (14-31), (14-34), and (14-49). However, the vibrational and electronic selection rules obtained in Chapter 14 must be reexamined for nonrigid molecules since the zero order wavefunction is different from that used in Eq. (14-18).

The zero order *roconvibronic* wavefunctions for a molecule with one contortional coordinate are of the form

$$\Phi_{\mathrm{rcve}} = \Phi_{\mathrm{rot}}(\theta\phi\chi)\Phi_{\mathrm{con}}(\rho)\Phi_{\mathrm{vib}}\Phi_{\mathrm{elec}}^{(e,S,m_S)}, \tag{15-23}$$

where here Φ_{vib} involves $3N - 7$ coordinates. The rotational quantum numbers involved will be J, k, and m for symmetric or spherical tops and J, K_a, K_c, and m for asymmetric tops; we use k_i for the contortional quantum number.

The selection rules are obtained by considering the conditions under which the following is true [from Eq. (14-19)]

$$\left\langle \Phi'_{\mathrm{rot}}\Phi'_{\mathrm{con}}\Phi'_{\mathrm{vib}}\Phi_{\mathrm{elec}}^{(e',S',m'_S)}|\mu_{\mathrm{s}}^{(1,\sigma)}|\Phi''_{\mathrm{rot}}\Phi''_{\mathrm{con}}\Phi''_{\mathrm{vib}}\Phi_{\mathrm{elec}}^{(e'',S'',m''_S)}\right\rangle \neq 0. \qquad (15\text{-}24)$$

for $\sigma = 0, \pm 1$. The irreducible tensor operator $\mu_{\mathrm{s}}^{(1,\sigma)}$ is defined in Eq. (14-13).

As indicated above, we can use the techniques discussed in Chapter 14 to obtain, from the matrix element in Eq. (15-24), expressions for the line strength similar to those in Eqs. (14-33), (14-43), (14-48) and (14-50) [where we use Eq. (14-33) for completely separable wavefunctions, Eq. (14-43) if rotation-vibration and rotation-contortion interaction is taken into account, Eq. (14-48) if the effects of the electron spin are considered, and Eq. (14-50) if also the effects of the nuclear spin are accounted for]. The only difference between the line strength expressions derived for nonrigid molecules and those in Eqs. (14-33), (14-43), (14-48) and (14-50) is in the form of the vibronic matrix elements determining the line strength. For a rigid molecule these matrix elements are given by Eqs. (14-26) and (14-27). For a nonrigid molecule Eq. (14-26) is changed to

$$\begin{aligned}&\left\langle \Phi'_{\mathrm{con}}\Phi'_{\mathrm{vib}}\Phi_{\mathrm{elec}}^{(e',S',m'_S)}\left|\mu_{\mathrm{m}}^{(1,\sigma')}\right|\Phi''_{\mathrm{con}}\Phi''_{\mathrm{vib}}\Phi_{\mathrm{elec}}^{(e'',S'',m''_S)}\right\rangle\\ &\qquad = \left\langle \Phi'_{\mathrm{con}}\Phi'_{\mathrm{vib}}\left|\mu_{\mathrm{m}}^{(1,\sigma')}(e',e'')\right|\Phi''_{\mathrm{con}}\Phi''_{\mathrm{vib}}\right\rangle, \qquad (15\text{-}25)\end{aligned}$$

whereas Eq. (14-27) is still valid. In order that the matrix element in Eq. (15-25) can be nonvanishing, the vanishing integral rule requires

$$\Gamma'_{\mathrm{con}} \otimes \Gamma''_{\mathrm{con}} \otimes \Gamma'_{\mathrm{vib}} \otimes \Gamma''_{\mathrm{vib}} \otimes \Gamma'_{\mathrm{elec}} \otimes \Gamma''_{\mathrm{elec}} \supset \Gamma\left(\mu_{\mathrm{m}}^{(1,\sigma')}\right), \qquad (15\text{-}26)$$

which is the nonrigid-molecule version of Eq. (14-35). Equivalently, we can express this condition as in Eq. (14-37) to obtain

$$\Gamma'_{\mathrm{con}} \otimes \Gamma''_{\mathrm{con}} \otimes \Gamma'_{\mathrm{vib}} \otimes \Gamma''_{\mathrm{vib}} \otimes \Gamma'_{\mathrm{elec}} \otimes \Gamma''_{\mathrm{elec}} \supset \Gamma(T_\alpha) \qquad (15\text{-}27)$$

where $\alpha = x$, y, or z.

As we did in Eq. (14-38) we now introduce Cartesian components of the electronic transition moment function. For a rigid molecule in zero order we neglect the dependence of the electronic transition moments $\mu_\alpha(e', e'')$ on the vibrational displacements because the vibrational displacements are small, and only a very small region of the $\mu_\alpha(e', e'')$ around equilibrium is probed. If vibrational displacements become large (of the order of the vibrational coordinates themselves), either because the vibrational energy levels involved are highly excited or because the molecule is nonrigid then the dependence of the $\mu_\alpha(e', e'')$ on the coordinates that have a large amplitude cannot usually be neglected.

For a molecule with one contortional coordinate ρ, we replace Eq. (14-41) by

$$\mu_\alpha(e',e'') = \mu_\alpha^{(0)}(e',e'';\rho) + \sum_r \mu_\alpha^{(r)}(e',e'';\rho)Q_r + \frac{1}{2}\sum_{r,s} \mu_\alpha^{(r,s)}(e',e'';\rho)Q_rQ_s + \cdots , \tag{15-28}$$

where r and $s = 1$ to $3N - 7$. The electronic integral $\mu_\alpha(e',e'')$ is expressed as a Taylor expansion in the small-amplitude vibrational normal coordinates Q_r of one of the electronic states, but the expansion coefficients are no longer constants as they were in Eq. (14-41); they are allowed to depend on the large amplitude coordinate ρ. The MS group symmetry of $\mu_\alpha(e',e'')$ is given by Eq. (14-39), exactly as for a rigid molecule. For a nonrigid molecule the symmetry analysis outlined below Eq. (14-41) has to be revised if ρ is not totally symmetric in the MS group, since the expansion coefficients $\mu_\alpha^{(0)}(e',e'';\rho)$, $\mu_\alpha^{(r)}(e',e'';\rho)$, ..., will not necessarily be totally symmetric. We discuss this point below.

A rotation-contortion-vibration transition is allowed within the electronic transition $e' \leftarrow e''$ if

$$\sum_\alpha \langle\Phi'_{\rm rot}|\lambda_{\alpha\zeta}|\Phi''_{\rm rot}\rangle\langle\Phi'_{\rm con}|\mu_\alpha^{(0)}(e',e'';\rho)\langle\Phi'_{\rm vib}|\Phi''_{\rm vib}\rangle|\Phi''_{\rm con}\rangle \neq 0. \tag{15-29}$$

We say that an electronic transition of a nonrigid molecule is *electronically allowed* if the leading term $\mu_\alpha^{(0)}(e',e'';\rho)$ is Eq. (15-28) is nonvanishing, even if this term vanishes for ρ equal to its equilibrium value ρ_e. The contortional transitions of an electronically allowed transition have

$$\left\langle\Phi'_{\rm con}\left|\mu_\alpha^{(0)}(e',e'';\rho)\right|\Phi''_{\rm con}\right\rangle \neq 0. \tag{15-30}$$

Since $\mu_\alpha^{(0)}(e',e'';\rho)$ has the same MS group symmetry as $\mu_\alpha(e',e'')$, this condition requires

$$\Gamma'_{\rm elec} \otimes \Gamma''_{\rm elec} \otimes \Gamma'_{\rm con} \otimes \Gamma''_{\rm con} \supset \Gamma(T_\alpha) \tag{15-31}$$

and the strong vibronic transitions associated with the electronically allowed transition will satisfy

$$\Gamma'_{\rm vib} = \Gamma''_{\rm vib} \tag{15-32}$$

for the $3N - 7$ small amplitude vibrations. The MS group used here has to be appropriate for the simultaneous treatment of both electronic states involved. Applying Eq. (15-31) we see that, in an electronic transition, bands will be allowed that in the approximation of neglecting the ρ-dependence of $\mu_\alpha(e',e'')$ would be forbidden. These bands will have $\Delta k_i \neq 0$. A good example of this is provided by the $S_1 \leftarrow S_0$ electronic band system of the toluene molecule which is discussed in Section 15.4.3.

Similarly allowed rotation-contortion-vibration transitions within an electronic state e, say, must satisfy

$$\sum_{\alpha}\langle\Phi'_{\rm rot}|\lambda_{\alpha\zeta}|\Phi''_{\rm rot}\rangle\langle\Phi'_{\rm con}|[\mu_{\alpha}^{(0)}(e,e;\rho) + \sum_{r}\mu_{\alpha}^{(r)}(e,e;\rho)\langle\Phi'_{\rm vib}|Q_r|\Phi''_{\rm vib}\rangle]|\Phi''_{\rm con}\rangle \neq 0. \qquad (15\text{-}33)$$

We deduce the general symmetry rule for an allowed vibrational transition as

$$\Gamma'_{\rm vib}\otimes\Gamma''_{\rm vib}\otimes\Gamma'_{\rm con}\otimes\Gamma''_{\rm con}\supset\Gamma(T_\alpha), \qquad (15\text{-}34)$$

which should be compared to Eq. (14-70). Using the second term on the right hand side of Eq. (15-28) we obtain the conditions for an allowed contortion-vibration transition as

$$\langle\Phi'_{\rm vib}|Q_r|\Phi''_{\rm vib}\rangle \neq 0 \qquad (15\text{-}35)$$

together with Eq. (15-34). In the harmonic oscillator approximation Eq. (15-35) leads to

$$\Delta v_r = \pm 1. \qquad (15\text{-}36)$$

We see that for a nonrigid molecule, when we allow for contortional fine structure, vibrational fundamentals are allowed for normal modes that do not have the species of a translation. This arises from the fact that we are not neglecting the ρ dependence of $\mu_{\alpha}^{(r)}(e,e;\rho)$. This point is perhaps made clearer by reference to Fig. 15-1 which depicts the allowed contortional lines in a fundamental band for which the species of the normal coordinate is not that of a translation. Thus the $k_i = 0 \leftarrow 0$ subband, in the $v_r = 1 \leftarrow 0$ band shown, is forbidden. It is supposed that the contortional symmetries are such that $\Delta k_i = \pm 1$ transitions accompanying the $v_r = 1 \leftarrow 0$ band are allowed; these would be sum and difference bands if the molecule were rigid and the contortional energy separation large. Thus for the nonrigid molecule with small contortional energy level separations the $v_r = 1 \leftarrow 0$ band is allowed; it consists of contortional subbands that satisfies $\Delta k_i = \pm 1$. Rotational transitions are ignored in Fig. 15-1.

Pure rotation-contortion transitions (the nonrigid molecule analogue of a pure rotation transition in a rigid molecule) must satisfy

$$\sum_{\alpha}\langle\Phi'_{\rm rot}|\lambda_{\alpha\zeta}|\Phi''_{\rm rot}\rangle\langle\Phi'_{\rm con}|\mu_{\alpha}^{(0)}(e,e;\rho)|\Phi''_{\rm con}\rangle \neq 0. \qquad (15\text{-}37)$$

This leads to the symmetry selection rule

$$\Gamma'_{\rm con}\otimes\Gamma''_{\rm con}\supset\Gamma(T_\alpha), \qquad (15\text{-}38)$$

which is less restrictive than demanding a nonvanishing permanent dipole moment given by Eq. (14-85).

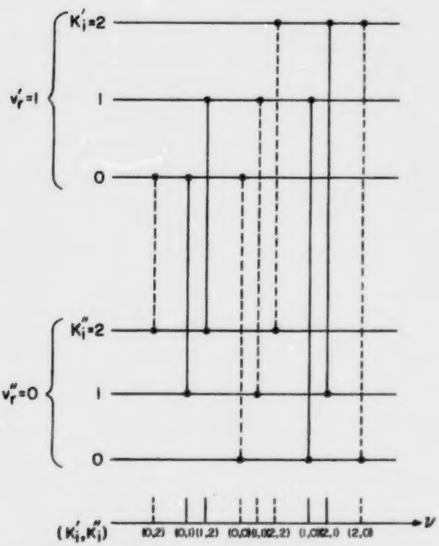

Fig. 15-1. The contortional fine structure ($\Delta K_i = \pm 1$) on a $v_r = 1 \leftarrow 0$ fundamental band for which $\Gamma(Q_r) \not\supset \Gamma(T_\alpha)$ but for which $\Gamma(Q_r) \otimes \Gamma[\Phi_{\mathrm{con}}(k_i)] \otimes \Gamma[\Phi_{\mathrm{con}}(k_i \pm 1)] \supset \Gamma(T_\alpha)$. The full lines are allowed transitions and the dotted lines are forbidden transitions. $K_i = |k_i|$. The rotational energy levels are omitted.

15.4 EXAMPLES

We discuss the application of these ideas to the nonrigid molecules ammonia NH_3, nitromethane CH_3NO_2, toluene $CH_3C_6H_5$, ethane CH_3CH_3, dimethylacetylene CH_3CCCH_3, hydrogen peroxide H_2O_2, ethylene C_2H_4, methylene CH_2, and H_2Te. These examples are chosen to illustrate various aspects of the spectroscopy and symmetry of nonrigid molecules. Ammonia is used as an example for determining the symmetry of rotation-inversion states, the selection rules for rotation-inversion transitions, and forbidden transitions. Nitromethane is introduced as an example for showing the effect of extra $J_\alpha J_\beta$ terms that can arise in the effective rotation-contortion Hamiltonian, and for showing how nonunique species for the normal coordinates can occur. Toluene provides an example that shows how forbidden torsional bands can occur in an electronic transition when allowance is made for the dependence of the transition moment on the torsional angle, and it also shows how we have to deal with the symmetry properties of the effective torsional potential function. Dimethylacetylene provides an example for introducing the extended molecular symmetry (EMS) group, and for showing how one deals with normal coordinates having nonunique symmetry species. Hydrogen peroxide is discussed in order to show how torsional tunneling can sometimes produce a staggering of energy levels rather than a splitting, and to show the use of energy level correlation diagrams. Ethylene demonstrates how one deals with the symmetry classification and selection rules in situations when two electronic states having different point group symmetry have to be considered together. Methylene shows how we deal with quasilinear molecules (for which an element of the $\boldsymbol{\mu}^{\mathrm{ref}}$ matrix is singular). Finally H_2Te provides an example of nonrigidity caused by strong centrifugal forces in highly excited rotational states; we discuss how the definition of the molecular symmetry group can be extended to describe such states.

NOTATION

For nonrigid molecules the notation used in the literature for labeling the rotation-contortion-vibration energy levels is not entirely consistent. The different types of contortion that can occur, such as internal rotation, inversion, bending and pseudorotation, the different axis system definitions (PAM, RAM, IAM), and the variations in the magnitude of the contortional splittings between molecules, and between different energy regions in the same molecule, probably make it impossible to develop a simple single consistent set of rotational, contortional and vibrational quantum number labels that are useful for describing the spectra, the interactions and the selection rules for all molecules. It should at least be universal to always use the irreducible representations of the appropriate MS group, or EMS group, for symmetry labeling the levels. Unfortunately, for historical reasons, even this is not the case for some molecules. To understand the existing literature for such molecules one has to learn the 'special' symmetry ideas that have been developed for it, and in this circumstance it is a moot point whether using the MS group labels will help or confuse by adding alternative labels. However, since the MS group is always the correct group to use for labeling distinguishable energy levels (by definition), it is necessary to check the results obtained using the 'special' symmetry by using the MS group. The nitromethane molecule below provides an example of where the historic 'special' symmetry group leads to error. As a general principle molecular energy levels exhibit a hierarchy of clustering patterns: nuclear-spin energy levels cluster together in each rotational state, rotational energy levels cluster together in each vibrational state, and vibrational energy levels cluster together in each electronic state. The development of approximately separable Hamiltonians and of useful near quantum number labels is based on this fact. However, contortional energy levels do not usually fit neatly into this hierarchy and we cannot, in general, label them as rotations or vibrations. For the examples we discuss below the notation used is as follows:

(a) The rotations

The rotational quantum number labels are generally based on the use of the appropriate molecular rotation group. This does not appear to lead to any particular difficulties for nonrigid molecules. The identity of the rotational quantum number k and the vibrational angular momentum quantum number l for a quasilinear molecule is discussed in Section 17.5.2.

(b) The contortions.

We suggest the use of the triple label ($v_{\mathrm{high}}, v_{\mathrm{low}}, \Gamma_{\mathrm{con}}$) on contortional energy levels where v_{high} is the vibrational quantum number in the high (insuperable contortional barrier) limit, v_{low} is the appropriate quantum number in the zero barrier limit, and Γ_{con} is the MS group symmetry species of the contorsional energy level in the low barrier MS group.[4] This is somewhat akin to the label ($N,J,\Gamma_{\mathrm{rve}}$) used on rotational energy levels of multiplet electronic states. For example, for ammonia, we use the label ($v_2, v_{\mathrm{inv}}, \Gamma_{\mathrm{inv}}$) for the inversion states; in the high barrier situation (or in a low resolution spectrum) v_2 is more useful, whereas v_{inv} is needed if the inversion splitting is resolved. The v_{inv} label leads directly to the MS group symmetry label Γ_{inv}. For nitromethane and dimethylacetylene the label k_i (with $K_i = |k_i|$) is used to label low barrier internal-rotation states.[5] We advocate the universal adoption of k_i as the internal rotation quantum number with $K_i = |k_i|$; it is used in Herzberg (1991a, 1991b), but unfortunately in the literature letters such as m or l are sometimes used (these are already 'reserved' as magnetic and vibrational angular momentum quantum numbers, respectively). In hydrogen peroxide the torsional barrier is much higher; our proposed notation for the torsional states would be (v_4, K_i, Γ) where Γ is the symmetry of the torsional level in the fully torsionally tunneling molecule. The historic τ notation used for hydrogen peroxide is essentially the same as this Γ label. Choosing Γ to be a number that is keyed to the MS group symmetry labels (as we do below) would then parallel the traditional use of the label τ.

(c) The vibrations.

The normal coordinates of a nonrigid molecule are functions of the contortional coordinate (or coordinates) and this often leads to the situation that the symmetry species of the normal coordinates is not fixed; it can depend on the way the force constants vary with the contortional coordinate (or coordinates). This makes it difficult to number the normal modes and to state their symmetry. One possible way to achieve an unambiguous symmetry, and numbering of the vibrations, is to define the symmetry and the numbering for a special choice of the symmetry coordinates. For nitromethane we choose symmetry coordinate that are independent of the torsional angle (see Table 15-5), and for dimethylacetylene in Table 15-10 we use degenerate symmetry coordinates that remain *cis* and *trans* coupled for all values of the torsional angle. Another much less serious source of confusion can arise depending on whether the contortion is included with the vibrations when we number them. It is probably best to include the contortion with the vibrations for the purpose of making the vibrational numbering, even if this leads to the situation exemplified in Table 15-5 for nitromethane, and in Table 15-10 for dimethylacetylene, of there being a 'missing' vibrational number.

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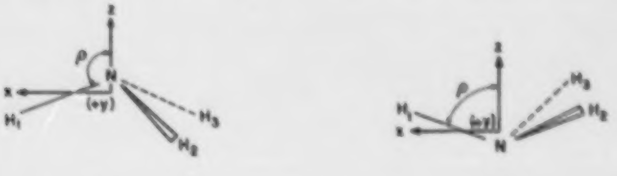
[4] One might wish to add the symmetry species in the high (insuperable) barrier MS group.

[5] For convenience we often use the word 'torsion' to describe the internal rotation motion in a low barrier case as well as the torsional motion in a high barrier case.

15.4.1 Ammonia

An ammonia molecule in its equilibrium configuration is shown in Fig. 15-2, and inversion between the two configurations shown in the figure gives rise to observable splittings in the spectrum. The inversion potential and inversion energy levels for $^{14}NH_3$ are shown in Fig. 15-3 [see Špirko and Kraemer (1989)]. In this figure the inversion barrier height is the barrier height in the effective inversion potential $V_{\text{eff}}(\rho)$ of $^{14}NH_3$ averaged over the zero point motion of the three high frequency vibrations ν_1, ν_3 and ν_4 [see Eq. (15-82)]. The barrier height in the Born-Oppenheimer potential surface $V_0(\rho)$ is 1885 cm^{-1} [see Fit III in Table II of Špirko and Kraemer (1989)]. If the effects of inversion tunneling were not observable the energy level situation would be as shown in Fig. 15-4. NF_3 is an example of such a case and the states of the umbrella vibration are labeled $v_2 = 0, 1, 2, \ldots$. The MS group of NF_3 is $\boldsymbol{C}_{3v}(\mathrm{M})$ and that of inverting NH_3 is $\boldsymbol{D}_{3h}(\mathrm{M})$; the character table of the $\boldsymbol{D}_{3h}(\mathrm{M})$ group is given in Table A-10. In Fig. 15-3 we number the inversion states by the v_2 value for the rigid molecule level with which they correlate and also with the quantum number v_{inv}. The use of the quantum number v_{inv} (which gives the total number of nodes in the inversion wavefunction) is preferable to v_2 for NH_3, particularly for the higher vibrational states, and it allows us to treat NH_3 as a planar molecule with a highly anharmonic out-of-plane vibration. Using this quantum number the vibrational and rotational selection rules for allowed optical transitions and perturbations are easy to formulate.



(a) (b)

Fig. 15-2. The reference configuration of NH_3. The NH bond lengths are equal to their equilibrium values and the three HNH angles are equal to each other. The molecule fixed (x, y, z) axes are the principal inertial axes.

It is first necessary to define the reference configuration, the orientation of the molecule fixed axes in the reference configuration, and the inversion angle ρ of the reference configuration. The reference configuration of the ammonia molecule is defined as having all three NH bond lengths equal to their equilibrium values and all three HNH angles equal to each other. The molecule fixed (x, y, z) axes are chosen to be right handed and to be the principal axes of the reference configuration, as indicated in Fig. 15-2. The positive z axis direction is defined as that direction a right handed screw would travel if twisted in the direction $H_1 \rightarrow H_2 \rightarrow H_3$, and the x axis is in the z-N-H_1 plane. The inver-

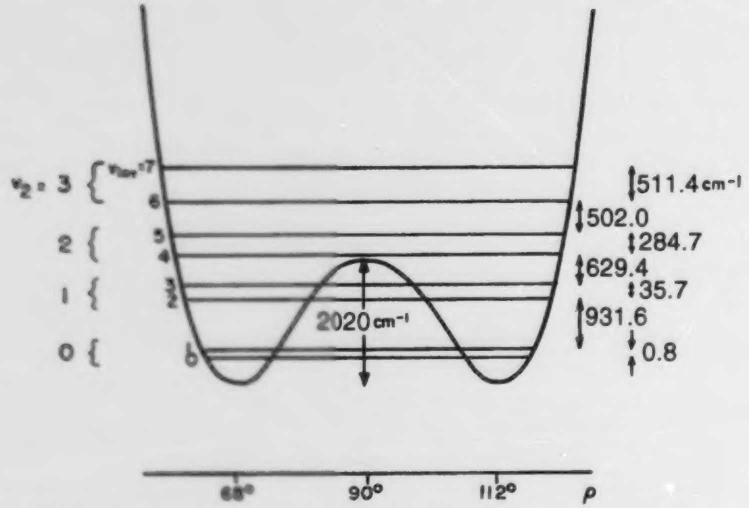
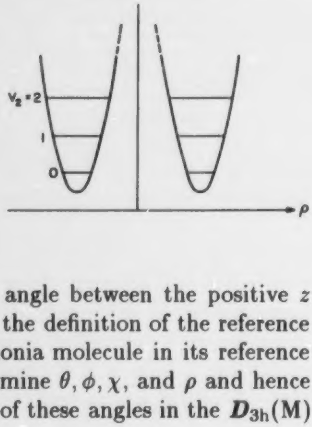


Fig. 15-3. The inversion energy levels and effective inversion potential of $^{14}NH_3$.

Fig. 15-4. The potential function and umbrella vibration energy levels of a rigidly C_{3v} molecule such as NF_3. The abscissa is the inversion coordinate.



sion angle in the reference configuration is the angle between the positive z axis direction and an NH bond. This completes the definition of the reference configuration. For an arbitrarily oriented ammonia molecule in its reference configuration we can use this definition to determine θ, ϕ, χ, and ρ and hence we can determine the transformation properties of these angles in the $\boldsymbol{D}_{3h}$(M) group.

There is confusion in some of the literature about the transformation of molecule fixed axes, and molecule fixed coordinates, under 'sense reversing' symmetry operations such as the E^* operation, and the correct discussion was first given by Hougen (1963). The molecule fixed axes are defined to be right handed when the molecule is in its reference configuration, just as they are when the molecule in an arbitrary distorted configuration. The operation E^* does not invert the molecule fixed axes of the NH_3 molecule. It rotates them. No operation of any molecular symmetry group of any molecule inverts the molecule fixed axes. When the molecule is not in its reference configuration the Eckart and Sayvetz conditions are used to obtain θ, ϕ, χ, and ρ; the Euler angles give the orientation of the right-handed (x, y, z) axes.

The rotation-inversion Hamiltonian of the ammonia molecule is particularly simple since by choosing the axes of the reference configuration as principal axes all off-diagonal elements of $\boldsymbol{\mu}^{\mathrm{ref}}$ vanish, and also for all values of ρ the reference configuration remains a symmetric top with $\mu_{xx}^{\mathrm{ref}} = \mu_{yy}^{\mathrm{ref}}$. The rotation-inversion Hamiltonian is

$$\hat{H}_{\mathrm{ri}} = \frac{1}{2}\mu_{xx}^{\mathrm{ref}}(\hat{J}_x{}^2 + \hat{J}_y{}^2) + \frac{1}{2}\mu_{zz}^{\mathrm{ref}}\hat{J}_z{}^2 + \frac{1}{2}\hat{J}_\rho\mu_{\rho\rho}^{\mathrm{ref}}\hat{J}_\rho + U(\rho) + V_0(\rho). \tag{15-39}$$

It is easy to solve the corresponding Schrödinger equation by writing a general solution as $|J, k, m\rangle|v_{\mathrm{inv}}\rangle$ where $|J, k, m\rangle$ is a symmetric top function and $|v_{\mathrm{inv}}\rangle$ is an inversion function of ρ that remains to be determined. Acting on the left of this function with $\langle J, k, m|\hat{H}_{\mathrm{ri}}$ and integrating out the Euler angles we obtain the rotation-inversion energy levels by solving

$$\left\{\frac{1}{2}\hat{J}_\rho\mu_{\rho\rho}^{\mathrm{ref}}\hat{J}_\rho + U(\rho) + V_0(\rho) + \frac{\hbar^2}{2}\{\mu_{xx}^{\mathrm{ref}}[J(J+1) - K^2] \right.$$
$$\left. + \mu_{zz}^{\mathrm{ref}}K^2\}\right\}|v_{\mathrm{inv}}; (J, K)\rangle = E_{\mathrm{ri}}|v_{\mathrm{inv}}; (J, K)\rangle. \tag{15-40}$$

This is a one dimensional inversion equation that is easy to solve numerically. This equation is solved for each J, K value and the terms in J and K enter as a rotationally dependent correction to the potential function. One can imagine the molecule as inverting in a given rotational state with a 'rotation-state-dependent' inversion potential. The inversion wavefunctions are then labeled with the appropriate J, K rotational quantum numbers. Each inversion state v_{inv} has a set of symmetric top energy levels built up on it.

The transformation properties of the rotational eigenfunctions $|J, k, m\rangle$ in $\boldsymbol{D}_{3\mathrm{h}}(\mathrm{M})$ can be determined using the equivalent rotations indicated in Table A-10, and the results in Eqs. (12-46) and (12-47). The inversion Hamiltonian can be diagonalized for any shape of $V_0(\rho)$ by numerical methods. For determining the symmetry of the eigenfunctions Γ_{inv} we can take $V_0(\rho)$ as being harmonic and centered on the planar configuration. Doing this we see [from Eq. (12-55) and the results after it] that the states with v_{inv} even are totally symmetric in $\boldsymbol{D}_{3\mathrm{h}}(\mathrm{M})$ and that the states with v_{inv} odd have the same symmetry as ρ; ρ has the symmetry A_2''. We can therefore write the species of the inversion states as

$$\Gamma(\Phi_{\mathrm{inv}}) = [A_2'']^{v_{\mathrm{inv}}}. \tag{15-41}$$

The species of the rotational states are given in Table 15-1. In the $\boldsymbol{C}_{3\mathrm{v}}$ group of any nonplanar conformation of the reference configuration the (small amplitude) normal coordinate representation (excluding the inversion) is $A_1 \oplus 2E$, and in the $\boldsymbol{D}_{3\mathrm{h}}$ group of the planar conformation it is $A_1' \oplus 2E'$. However, the MS group $\boldsymbol{D}_{3\mathrm{h}}$ is isomorphic to the point group of the planar conformation which means that the normal coordinate species in the MS group is uniquely given by[6]

$$\Gamma(Q) = A_1' \oplus 2E'. \tag{15-42}$$

By the same reasoning the electron spin–orbit wavefunction of the ground state of NH_3 is totally symmetric in $\boldsymbol{D}_{3h}(M)$ which means that the rotation-inversion-vibronic species of the ground electronic state levels of ammonia can be obtained from the results in Table 15-1 together with Eqs. (15-41) and (15-42).

Table 15-1

Symmetry species of rotational states of NH_3 in $\boldsymbol{D}_{3h}(M)$[a]

K		Γ_{rot}
0	(J even)	A_1'
	(J odd)	A_2'
$6n \pm 1$		E''
$6n \pm 2$		E'
$6n + 3$		$A_1'' \oplus A_2''$
$6n + 6$		$A_1' \oplus A_2'$

[a] n is a nonnegative integer and $K \geq 0$.

Having determined the symmetry species of the rotational, inversion, and vibrational states of the molecule the selection rules for allowed electric dipole transitions can be determined. The selection rules for transitions between the rotation-inversion states are particularly important. From Table A-10 we see that the species of T_z is A_2'', that of (T_x, T_y) is E', and that of Γ^* is A_1''. Thus the E' fundamentals will be infrared active with selection rules $\Delta K = \pm 1$ and $\Delta J = 0, \pm 1$, and the rotation-inversion spectrum will satisfy the selection rules $\Delta K = 0$, $\Delta v_{\rm inv} =$ odd with $\Delta J = 0, \pm 1$. Since the $v_{\rm inv} = 1$ inversion state is very close to the $v_{\rm inv} = 0$ state, hot transitions from it will be as important as those from the ground ($v_{\rm inv} = 0$) state. In Fig. 15-5 the lowest rotational levels of the $v_{\rm inv} = 0, 1, 2$, and 3 states are drawn, and some of the rotation-inversion transitions allowed in the electric dipole absorption spectrum are marked by solid lines. The $v_{\rm inv} = 3 \leftarrow 0$ and $v_{\rm inv} = 2 \leftarrow 1$ bands are completely on top of each other in the infrared spectrum, and these bands correlate with the $v_2 = 1 \leftarrow 0$ band of the rigid nonplanar molecule. In the microwave spectrum $v_{\rm inv} = 1 \leftarrow 0$ and $v_{\rm inv} = 0 \leftarrow 1$ transitions occur in absorption, and three of these types of transition are also marked in Fig. 15-5; these correlate with pure rotation transitions of the rigidly nonplanar molecule.

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[6] The inversion is ν_2 and the vibrations are numbered $\nu_1(A_1')$, $\nu_3(E')$ and $\nu_4(E')$.

Forbidden transitions are also indicated in Fig. 15-5. Rotational transitions within the $v_{\rm inv} = 0$ or 1 states are forbidden, but rotation-vibration interaction makes such forbidden transitions weakly allowed with $\Delta k = \pm 3$ selection rules (as discussed for H_3^+ in Section 14.1.14); four of these transitions are indicated by a dashed line in Fig. 15-5 [see Oka, Shimizu, Shimizu and Watson (1971b) and Oka (1976)]. The $v_{\rm inv} = 2 - 0$ and $3 - 1$ forbidden bands also gain intensity (with the same selection rules on k) by such interactions and three of these transitions, in the $v_{\rm inv} = 2 - 0$ band, are also marked by a dashed line in the figure. In an electric field (i.e., in the Stark effect) rovibrational states connected by the species A_1'' with $\Delta J = 0$ or ± 1 are mixed. In particular states with the same K value and with $v_{\rm inv}$ values differing by one will be mixed by an electric field, and as a result forbidden transitions with $\Delta v_{\rm inv}$ even will steal intensity from allowed transitions having $\Delta v_{\rm inv}$ odd; such transitions will have $\Delta K = 0$. Two examples of such a forbidden transition made allowed by applying an electric field are indicated by a dot-dash line in Fig. 15-5.

The nuclear spin states and the nuclear spin statistical weights for $^{14}NH_3$ are discussed in Chapter 8 [see Eq. (8-9) and Table 8-6] and in Section 13.6.2. Rotational levels of species A_1' and A_1'' are missing, the levels of species A_2' and A_2'' can be in the 12 nuclear spin states of species A_1' (and therefore they have a nuclear spin statistical weight of 12), and the levels of species E' or E'' can be in the 6 nuclear spin states of species E' (and therefore they have a nuclear spin statistical weight of 6). As already indicated for H_2 and CH_3F in Section 13.6.3, the levels with the greater nuclear spin statistical weight (the A_2' and A_2'' levels) are called the ***ortho*** levels and the levels with the lesser nuclear spin statistical weight (the E' and E'' levels) the ***para*** levels. We see that all the transitions indicated in Fig. 15-5 are para-para ($E' \leftrightarrow E''$ in the absence of an external field) transitions. We could have indicated some ortho-ortho transitions ($A_2' - A_2''$) such as $(v_{\rm inv}, J, K) = (3,0,0) - (0,1,0)$ but we did not want to overburden the figure. What about ortho-para transitions that involve a change in nuclear spin state? Just as for BF_3 in Problem 8-1 the complete internal wavefunction of NH_3 can only be of species A_2' or A_2'' in $\boldsymbol{D}_{3h}(M)$ as the parity of $\Phi_{\rm int}$ is + or −. Rotational levels of species E' have to be in nuclear spin states of species E',and rotational levels of species A_2' have to be in nuclear spin states of species A_1'. As a result E' and A_2' rotational levels produce hyperfine $\Phi_{\rm int}$ states of species A_2' (+ parity levels). Similarly E'' and A_2'' levels produce $\Phi_{\rm int}$ states of species A_2'' (− parity levels). Thus ortho-para mixing can mix E' and A_2' rotational levels, and separately it can mix E'' and A_2'' levels. Allowing for ortho-para mixing, and using the rigorous selection rule that parity must change in an allowed transition [see Eq. (14-10)], we see that ortho-para transitions will connect rotational levels $E' \leftrightarrow A_2''$ and $E'' \leftrightarrow A_2'$ [with the rigorous selection rule $\Delta F = 0, \pm 1$ from Eq. (14-11)]. The transitions $E' - A_2'$ and $E'' - A_2''$ are strictly forbidden as electric dipole transitions in an isolated ammonia molecule in field free space since they do not involve a change of parity. In an electric field they become allowed since parity is not then conserved.

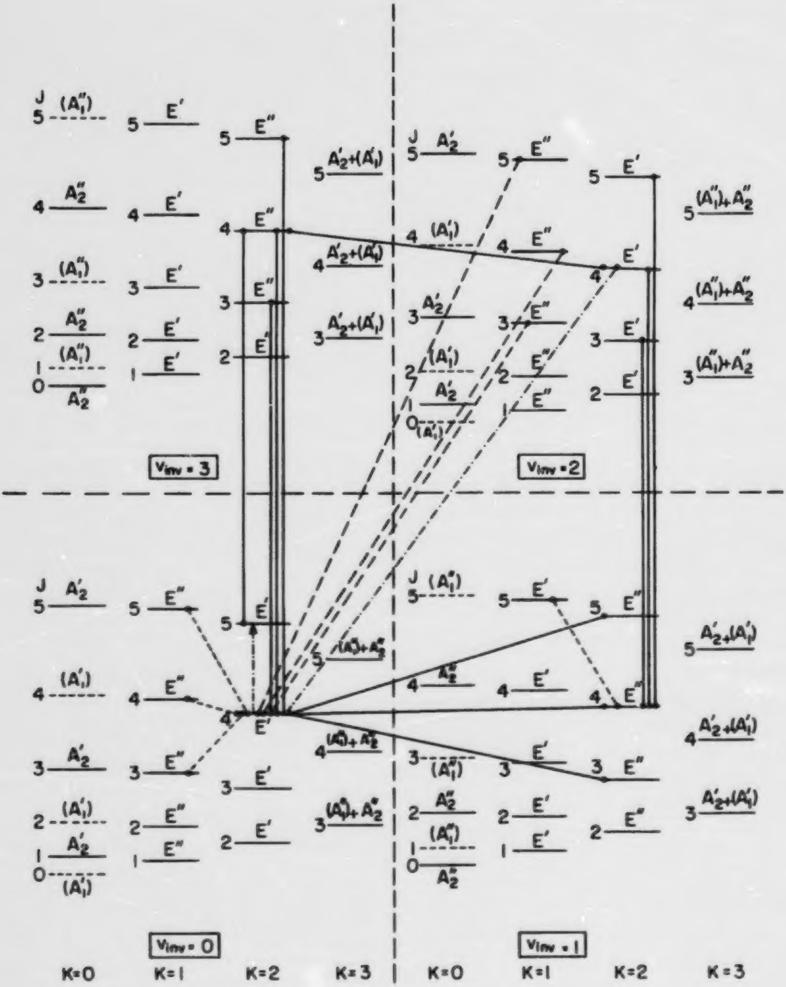

J
5 (A₁″)
4 A₂″
3 (A₁″)
2 A₂″
1 (A₁″)
0 A₂″
5 E′
4 E′
3 E′
2 E′
1 E′
5 E″
4 E″
3 E″
2 E″
5 A₂′+(A₁′)
4 A₂′+(A₁′)
3 A₂′+(A₁′)
J
5 A₂′
4 (A₁′)
3 A₂′
2 (A₁′)
1 A₂′
0 (A₁′)
5 E″
4 E″
3 E″
2 E″
1 E″
5 E′
4 E′
3 E′
2 E′
5 (A₁″)+A₂″
4 (A₁″)+A₂″
3 (A₁″)+A₂″
V_inv = 3
V_inv = 2
J
5 A₂′
4 (A₁′)
3 A₂′
2 (A₁′)
1 A₂′
0 (A₁′)
5 E″
4 E″
3 E″
2 E″
1 E″
5 E′
4 E′
3 E′
2 E′
5 (A₁″)+A₂″
4 (A₁″)+A₂″
3 (A₁″)+A₂″
J
5 (A₁″)
4 A₂″
3 (A₁″)
2 A₂″
1 (A₁″)
0 A₂″
5 E′
4 E′
3 E′
2 E′
1 E′
5 E″
4 E″
3 E″
2 E″
5 A₂′+(A₁′)
4 A₂′+(A₁′)
3 A₂′+(A₁′)
V_inv = 0
V_inv = 1
K=0
K=1
K=2
K=3
K=0
K=1
K=2
K=3

Fig. 15-5. The lower rotational energy levels of the $(v_2, v_{\rm inv}, \Gamma_{\rm inv}) = (0,0,A_1')$, $(0,1,A_2'')$, $(1,2,A_1')$ and $(1,3,A_2'')$ states of NH_3. The $\boldsymbol{D}_{3h}$(M) symmetry labels $\Gamma_{\rm rve}$ have been added and rovibronic states forbidden by nuclear spin statistics are in parentheses. Some of the allowed transitions are marked and a full line is used; these transitions satisfy $\Delta v_{\rm inv}$ = odd and $\Delta K = 0$. Using a dashed line some of the forbidden transitions made allowed by rotation-vibration interaction are marked and these have $\Delta v_{\rm inv}$ = even, $\Delta k = 3$. Both of these types of transition occur with $\Delta J = 0$ or ± 1. Forbidden transitions made allowed by applying an external electric field (these transitions are allowed two-photon transitions) have selection rules $\Delta v_{\rm inv}$ = even, $\Delta K = 0$, and $\Delta J = 0$, ± 1, and ± 2; two of these transitions are marked by a dot-dash line.

15.4.2 Nitromethane

In Fig. 15-6 the nitromethane molecule is shown in its reference configuration: all bond lengths and angles have their equilibrium values (except the torsional angle ρ), and the molecule fixed axes are located (using PAM) as principal axes with the z axis is in the C $\rightarrow$ N direction and the x axis is in the CNO_4 plane. The torsional angle ρ is the dihedral H_1CNO_4 angle measured from CH_1 in a right handed sense about the z axis. This molecule has practically free internal rotation, and its MS group is the group $\boldsymbol{G}_{12}$ which is isomorphic to the $\boldsymbol{D}_{3h}$ group. Following the notation of Table 1 in Longuet-Higgins (1963), who considered the CH_3BF_2 molecule, the character table of $\boldsymbol{G}_{12}$ is given in Table A-24. It is easy to see that the only nonvanishing elements of the $\boldsymbol{\mu}^{\mathrm{ref}}$ are the xx, yy, zz, $\rho\rho$ and the $z\rho = \rho z$ elements. Also all of these elements are independent of ρ.

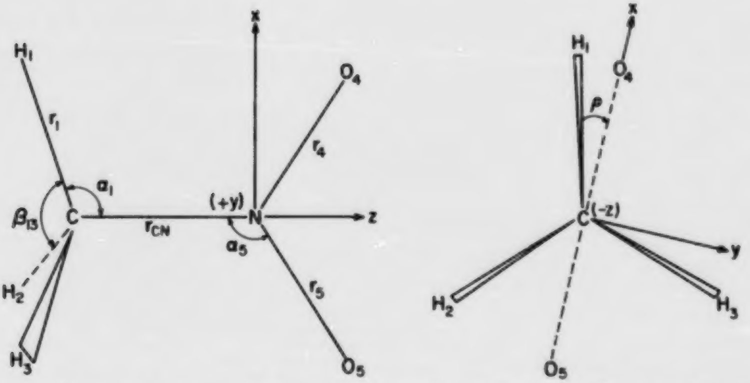


Fig. 15-6. The reference configuration of CH_3NO_2. All bond lengths and angles, except the torsional angle ρ, have their equilibrium values, and the molecule fixed (x, y, z) axes are the principal inertial axes.

Before discussing the rotation-torsion Hamiltonian and the symmetry species of the rotational, torsional and vibrational wavefunctions in $\boldsymbol{G}_{12}$ we briefly look at the nuclear spin statistical weights of CH_3NO_2 and CH_3BF_2. Using Eq. (8-28) we determine that for $^{12}CH_3{}^{14}N^{16}O_2$

$$\Gamma^{\mathrm{sw}}_{\mathrm{rve}} = 12A_1' \oplus 12A_2' \oplus 12E', \tag{15-43}$$

and for $^{12}CH_3{}^{11}B^{19}F_2$ we have

$$\Gamma^{\mathrm{sw}}_{\mathrm{rve}} = 16A_1' \oplus 16A_2' \oplus 16E' \oplus 48A_1'' \oplus 48A_2'' \oplus 48E''. \tag{15-44}$$

Because of the zero spin of the ^{16}O nucleus the levels that are antisymmetric in the operation (45), i.e., levels of symmetries A_1'', A_2'', and E'', are missing for $CH_3N^{16}O_2$. In CH_3BF_2 there is a 1:3 intensity alternation depending on the symmetry under (45). The results given here for CH_3BF_2 accord with those given by Longuet-Higgins (1963) when allowance is made for the fourfold degeneracy of the $I = 3/2$ ^{11}B nucleus.

The zero order rotation-torsion PAM Hamiltonian for nitromethane is

$$\hat{H}_{\mathrm{rt}} = \frac{1}{2}\mu_{xx}^{\mathrm{ref}}\hat{J}_x{}^2 + \frac{1}{2}\mu_{yy}^{\mathrm{ref}}\hat{J}_y{}^2 + \frac{1}{2}\mu_{zz}^{\mathrm{ref}}\hat{J}_z{}^2 + \frac{1}{2}\mu_{\rho\rho}^{\mathrm{ref}}\hat{J}_\rho^2 + \mu_{z\rho}^{\mathrm{ref}}\hat{J}_z\hat{J}_\rho + V_0(\rho), \tag{15-45}$$

where none of the $\mu_{\alpha\beta}^{\mathrm{ref}}$ elements depend on ρ. To diagonalize this Hamiltonian we use a basis set of symmetric top and free internal rotor functions. If the torsional barrier is ignored then the only off-diagonal matrix elements are the asymmetric rotor $\Delta K_a = \pm 2$ matrix elements. The zero-barrier eigenfunctions are thus the simple product of asymmetric top rotor functions and free internal rotor torsional functions. From the equivalent rotations given in Table A-24 we deduce the asymmetric rotor species to be those in Table 15-2. This molecule is a near oblate top ($I_{aa} \approx I_{bb} < I_{cc}$) and the asymmetric top rotational energy levels can be determined in the usual way using a $|J, k_c\rangle$ basis. Longuet-Higgins (1963) classified the $|J, k_c\rangle$ symmetric top functions as being of species $A_2'\oplus A_2''$ for K_c odd and $A_1'\oplus A_1''$ for K_c even, which is correct.

Table 15-2

Species of asymmetric top rotational wavefunctions of CH_3NO_2 in the group G_{12}

K_aK_c	Γ_{rot}	K_aK_c	Γ_{rot}
ee	A_1'	oe	A_1''
eo	A_2'	oo	A_2''

The zero barrier torsional wavefunctions are the eigenfunctions of $\frac{1}{2}\mu_{\rho\rho}^{\mathrm{ref}}\hat{J}_\rho^2$ with the boundary condition that $\Phi_{\mathrm{tor}}(\rho + 2\pi) = \Phi_{\mathrm{tor}}(\rho)$. Thus the torsional eigenfunctions and eigenvalues (in cm^{-1}) are given by:

$$\Phi_{\mathrm{tor}} = \exp(ik_i\rho) \tag{15-46}$$

and

$$E_{\mathrm{tor}} = \frac{\hbar^2}{2hc}\mu_{\rho\rho}^{\mathrm{ref}}k_i{}^2 = Fk_i{}^2, \tag{15-47}$$

respectively, where $k_i = 0, \pm 1, \pm 2, \ldots$, and F is the rotational constant (in cm^{-1}) of the CH_3 group about the CN axis. The transformation properties of ρ

Table 15-3

Species of torsional wavefunctions, $\Phi_{\text{tor}}^{(\pm)}$, of CH_3NO_2 in the MS group G_{12}[a]

K_i	Γ
0	A_1'
$6n \pm 1$	E''
$6n \pm 2$	E'
$6n + 3\ (+)$	A_1''
$6n + 3\ (-)$	A_2''
$6n + 6\ (+)$	A_1'
$6n + 6\ (-)$	A_2'

[a] n is a nonnegative integer and $K_i = |k_i| \geq 0$.

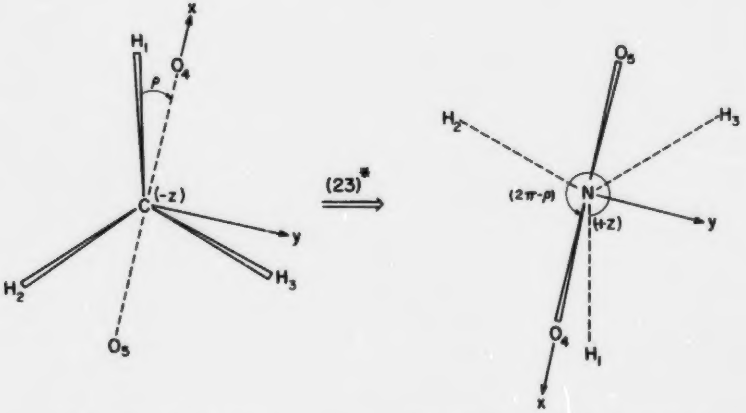


Fig. 15-7. The effect of the operation (23)* on the torsional angle of the reference configuration CH_3NO_2.

under the effect of the elements of G_{12} are determined from the transformations of the reference configuration to be

$$\begin{aligned}(123)\rho &= \rho - (2\pi/3),\\ (23)^*\rho &= 2\pi - \rho,\\ (45)\rho &= \rho + \pi,\\ (123)(45)\rho &= \rho + (\pi/3),\\ (23)(45)^*\rho &= \pi - \rho.\end{aligned} \tag{15-48}$$

The effect of $(23)^*$ is depicted in Fig. 15-7. Since $(23)^*$ changes ρ to $-\rho$ torsional functions that transform irreducibly in the MS group, for all $K_i = |k_i|$ values, are

$$\Phi_{\text{tor}}^{(\pm)} = [\exp(ik_i\rho) \pm \exp(-ik_i\rho)]/(2\sqrt{\pi}). \tag{15-49}$$

These functions are normalized to unity. The species of the torsional functions depend on K_i and on ($\pm$) as shown in Table 15-3. Note that $\Phi_{\text{tor}}^{(+)}$ is $(1/\sqrt{\pi})\cos k_i\rho$ and $\Phi_{\text{tor}}^{(-)}$ is $(i/\sqrt{\pi})\sin k_i\rho$. This means that Table 15-3 can be used to obtain the species of the functions $\sin n\rho$ and $\cos n\rho$ which is useful.

The effect of introducing a torsional barrier leads to a very interesting conclusion. A completely general expansion for the torsional potential function would be as an expansion in $\sin n\rho$ and $\cos n\rho$ functions, i.e.,

$$V(\rho) = \sum_{n=0}^{\infty}(V_n \cos n\rho + W_n \sin n\rho)/2, \tag{15-50}$$

where V_n and W_n are constants. From Table 15-3 we can determine that the only terms in this series that are of symmetry $A_1{}'$, and which can therefore be present in the Hamiltonian, are the $\cos n\rho$ terms having $n = 6, 12, 18, \ldots$. Thus only the constants V_6, V_{12}, V_{18} etc. can be nonvanishing. Sørensen and Pedersen (1983) could fit the microwave spectrum of CH_3NO_2 to experimental precision by taking just the V_6 term. The value of V_6 is then the height of the torsional barrier. The effect of a V_6 term in $V(\rho)$ is to split the degeneracy of the $\Phi_{\text{tor}}^{(\pm)}$ levels for $K_i = 3$; in first order the $\Phi_{\text{tor}}^{(+)}$ state gets energy $9F + V_6/4$ and the $\Phi_{\text{tor}}^{(-)}$ gets energy $9F - V_6/4$. Sørensen and Pedersen (1983) determined that in the ground vibrational state the torsional barrier is 2.1 cm^{-1} for CH_3NO_2 and 1.8 cm^{-1} for CD_3NO_2. Adding this V_6 potential also adds off-diagonal Hamiltonian matrix elements having $\Delta k_i = \pm 6$. Changing the sign of V_6 (i.e., changing the equilibrium structure from being eclipsed to being staggered) has no effect on the rotation-torsion energies, and it would seem that the sign of the torsional barrier cannot be determined.

However, microwave spectroscopy is very precise, and a satisfactory fitting of the levels is only possible if we allow for the effect of the small amplitude vibrations. Thus we must use the effective rotation-contortion Hamiltonian in which, as well as quartic centrifugal distortion terms, there are corrections to the terms quadratic in the $\hat{J}_\alpha$. Sørensen and Pedersen (1983) carefully studied the symmetry of various operators in $\boldsymbol{G}_{12}$. Using the results that $\cos 3\rho$ has symmetry $A_1{}''$ and $\sin 3\rho$ has symmetry $A_2{}''$ (see Table 15-3), together with the symmetries of the $\hat{J}_\alpha$ given in Table A-24, they show that the following rotation-torsion coupling term, which they call R_3, is totally symmetric in $\boldsymbol{G}_{12}$ and can therefore be present in the effective rotation-torsion Hamiltonian:

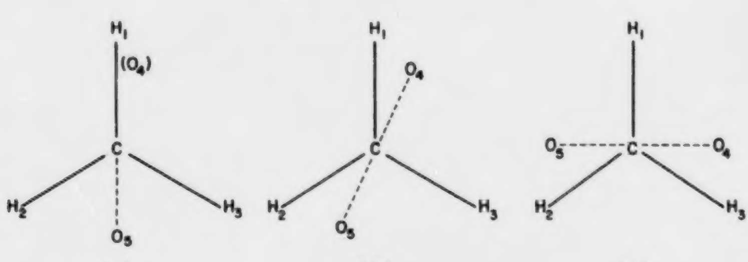
$$R_3 = k_b\hat{J}_b(\hat{J}_\rho \cos 3\rho + \cos 3\rho \hat{J}_\rho) + k_c\hat{J}_c(\hat{J}_\rho \sin 3\rho + \sin 3\rho \hat{J}_\rho), \tag{15-51}$$

which we can rewrite as

$$R_3 = \mu_{b\rho}^{\text{eff}}\hat{J}_b\hat{J}_\rho + \mu_{c\rho}^{\text{eff}}\hat{J}_c\hat{J}_\rho + \frac{1}{2}(\hat{J}_\rho\mu_{b\rho}^{\text{eff}})\hat{J}_b + \frac{1}{2}(\hat{J}_\rho\mu_{c\rho}^{\text{eff}})\hat{J}_c, \tag{15-52}$$

where $\mu_{b\rho}^{\text{eff}} = 2k_b\cos3\rho$ and $\mu_{c\rho}^{\text{eff}} = 2k_c\sin3\rho$ (where k_b and k_c are not rotational quantum numbers). Sørensen and Pedersen (1983) use the notation of Eq. (15-51), and Eq. (15-52) is the same term put into our notation. Not all possible $\hat{J}_\alpha \hat{J}_\beta$ terms allowed by symmetry in the effective rotation-contortion Hamiltonian have determinable coefficients [see Sørensen (1988, 1996)]. This is in the same sense that only five of the quartic centrifugal distortion constants can be determined for a general asymmetric top molecule (see page 353). The rotation-torsion coupling term R_3 mixes states that have k_i values differing by 3 and k_a values differing by 1. Sørensen and Pedersen (1983) were able to identify perturbations caused by this term in the microwave spectrum and hence confirm that $\boldsymbol{G}_{12}$ is indeed the correct symmetry group as proposed by Longuet-Higgins (1963) when he invented the MS group. The invariance group of the rotation-torsion Hamiltonian of Eq. (15-45) was used in an earlier study of CH_3BF_2 by Wilson, Lin and Lide (1955) and it is a group isomorphic to $\boldsymbol{D}_{6\text{h}}$ which is larger than $\boldsymbol{G}_{12}$ [see, for example, Table VIII in Lin and Swalen (1959)]; the term R_3 is not totally symmetric in this larger group. Sørensen and Pedersen (1983) show very clearly that it is not rigorous to start with an assumed form of the Hamiltonian and then to determine the invariance group of that Hamiltonian. Neglected terms in the complete Hamiltonian may break that symmetry. On the other hand the complete Hamiltonian of any isolated molecule in field free space has to be invariant to all the elements of the MS group.

In analyzing perturbations caused by the term R_3, given in Eq. (15-51) above, Sørensen and Pedersen (1983) were also able to determine the *sign* of V_6. This was an unexpected bonus. It could be proved that the minimum in the torsional potential occurs when the NO_2 group is staggered relative to the CH_3 group, i.e., when $\rho = \pi/2 + 2\pi n/6$ (see Fig. 15-6).



(a) (b) (c)

Fig. 15-8. Three rigid conformers of CH_3NO_2 having different symmetries.

To determine the species of the normal coordinates in $\boldsymbol{G}_{12}$ we consider the species of the normal coordinates of the molecule when it is rigidly in each of the three conformers shown in Fig. 15-8. Conformer (a) [in which the dihedral angle H_1CNO_4 is 0°] has MS group $\boldsymbol{G}_{\text{a}} = \{E, (23)^*\}$, conformer (b) [in which the dihedral angle H_3CNO_4 is somewhat larger than 90°] has MS group $\boldsymbol{G}_{\text{b}} = \{E\}$, and conformer (c) [in which the dihedral angle H_1CNO_4 is 90°] has MS group

$\boldsymbol{G}_c = \{E, (23)(45)^*\}$. The character tables of $\boldsymbol{G}_a$ and $\boldsymbol{G}_c$ are the same as that of $\boldsymbol{C}_s(\mathrm{M})$ given in Table A-2. Classifying the normal modes of each of these rigid conformers in its MS group (using the technique discussed in Chapter 12) and omitting the torsional species we obtain

$$\begin{aligned} \boldsymbol{G}_a: &\quad \Gamma(Q) = 10A' \oplus 4A'', \\ \boldsymbol{G}_b: &\quad \Gamma(Q) = 14A, \\ \boldsymbol{G}_c: &\quad \Gamma(Q) = 9A' \oplus 5A''. \end{aligned} \tag{15-53}$$

The correlation table of $\boldsymbol{G}_{12}$ with $\boldsymbol{G}_a$, $\boldsymbol{G}_b$ and $\boldsymbol{G}_c$ is given in Table 15-4, and by using this table with Eq. (15-53) we can determine that the species of the normal coordinates of free rotor CH_3NO_2 in the group $\boldsymbol{G}_{12}$. To do this let us initially say that this species is given by

$$\Gamma(Q) = pA_1' \oplus qA_2' \oplus rA_1'' \oplus lA_2'' \oplus mE' \oplus nE''. \tag{15-54}$$

For the $\boldsymbol{G}_a$ conformer the number of A' normal coordinates is 10, whereas the number of A'' normal coordinates is 4. Thus we must have (from the correlation of $\boldsymbol{G}_a$ and $\boldsymbol{G}_{12}$ species in Table 15-4) the restrictions

$$p + m + r + n = 10, \quad \text{and} \quad q + m + l + n = 4. \tag{15-55}$$

Similar considerations for the $\boldsymbol{G}_c$ conformer lead to the restrictions

$$p + m + l + n = 9, \quad \text{and} \quad q + m + r + n = 5. \tag{15-56}$$

Thus for a given choice of l, m and n these four equations lead to the result that

$$\begin{aligned} \Gamma(Q) = {} & (9 - l - m - n)A_1' \oplus (4 - l - m - n)A_2' \oplus (l + 1)A_1'' \oplus lA_2'' \\ & \oplus mE' \oplus nE'', \end{aligned} \tag{15-57}$$

where l, m, and n are integers satisfying

$$l \geq 0, \qquad m \geq 0, \qquad n \geq 0, \qquad (l + m + n) \leq 4. \tag{15-58}$$

The restrictions of Eq. (15-58) result from the fact that none of the coefficients in Eq. (15-57) can be negative. As a result of this there are 35 different possible normal coordinate species for nitromethane. A similar analysis for methanol CH_3OH, for which the species of the normal coordinates in the rigid $\boldsymbol{C}_s$ conformer is $8A' \oplus 3A''$ (excluding the torsion), yields the normal coordinate species in the $\boldsymbol{G}_6$ MS group (see Table A-22):

$$\Gamma(Q) = (8 - n)A_1 \oplus (3 - n)A_2 \oplus nE', \tag{15-59}$$

where n is an integer satisfying

$$0 \leq n \leq 3. \tag{15-60}$$

There are thus four different possible normal coordinate species for methanol. For acetaldehyde CH_3CHO, for which the species of the normal coordinates in the rigid C_s conformer is $10A' \oplus 4A''$ (excluding the torsion), the normal coordinate species in the $\boldsymbol{G}_6$ MS group is:

$$\Gamma(Q) = (10 - n)A_1 \oplus (4 - n)A_2 \oplus nE', \tag{15-61}$$

where n is an integer satisfying

$$0 \leq n \leq 4. \tag{15-62}$$

There are thus five different possible normal coordinate species for acetaldehyde [see Hougen (1997)].

Table 15-4
The correlation table of the MS group $\boldsymbol{G}_{12}$ for torsionally tunneling CH_3NO_2[a]

$\boldsymbol{G}_{12}$:	$\boldsymbol{G}_a$	$\boldsymbol{G}_b$	$\boldsymbol{G}_c$
A_1' :	A'	A	A'
A_2' :	A''	A	A''
E' :	$A' \oplus A''$	$2A$	$A' \oplus A''$
A_1'' :	A'	A	A''
A_2'' :	A''	A	A'
E'' :	$A' \oplus A''$	$2A$	$A' \oplus A''$

[a] The groups $\boldsymbol{G}_a$, $\boldsymbol{G}_b$, and $\boldsymbol{G}_c$ are for the rigid conformers of Fig. 15-8.

For nitromethane there are very many possibilities for the symmetry species of the small amplitude normal coordinates in the MS group. In general, for a nonrigid molecule, if the order of each of the rigid conformer point groups is less than that of the nonrigid molecule MS group then there will be multiple possibilities for the species of the small amplitude normal coordinates. This comes about because of the ρ-dependence of the normal coordinates.

To analyze in detail the vibrational spectrum, experience with dimethylacetylene (see below) leads us to suggest that the way to proceed would be to assume a particular form for the ρ dependence of the symmetry coordinates. One would then determine the $\boldsymbol{G}$ matrix for the chosen coordinates, and assume a ρ-independent $\boldsymbol{F}$ matrix in zero order. After calculating the rotation-torsion-vibration energy levels, and determining the selection rules on the rotational and torsional quantum numbers for vibrational transitions, the ρ dependence of the $\boldsymbol{F}$ matrix would be dealt with by perturbation theory or exact matrix diagonalization. If one were to completely neglect the ρ dependence of the normal coordinates then the normal coordinate representation of CH_3NO_2 is obtained as the species of the ρ independent symmetry coordinates given in Table 15-5. This species is

$$\Gamma^0(Q) = 5A_1{}' \oplus 2A_1{}'' \oplus A_2{}'' \oplus 3E' \tag{15-63}$$

[i.e., this has $l = 1$, $m = 3$, and $n = 0$ in Eq. (15-57)]. Note that the three perpendicular vibrations of the methyl group are doubly degenerate here; we have neglected the coupling of such vibrations with the NO_2 frame that arises from the $\boldsymbol{G}$ matrix and from the ρ dependence of the $\boldsymbol{F}$ matrix. It seems likely that such a description will be appropriate for states having high K_i. At low values of K_i the double degeneracies of the methyl group vibrations S_{10}, S_{11}, and S_{12} will be significantly split by interactions with the NO_2 frame into in-plane $S_r^{(\mathrm{i})}$ and out-of-plane $S_r^{(\mathrm{o})}$ modes, and if we wished to allow for this in zero order we would use symmetry coordinates

$$S_r^{(\mathrm{i})} = \cos\rho\, S_{ra} - \sin\rho\, S_{rb}, \qquad S_r^{(\mathrm{o})} = \sin\rho\, S_{ra} + \cos\rho\, S_{rb} \tag{15-64}$$

for $r = 10, 11$, and 12. $S_r^{(\mathrm{i})}$ is of species $A_1{}''$; and $S_r^{(\mathrm{o})}$ is of species $A_2{}''$ so that the symmetry coordinate representation is now

$$5A_1{}' \oplus 5A_1{}'' \oplus 4A_2{}'' \tag{15-65}$$

[i.e., $l = 4$ and $m = n = 0$ in Eq. (15-57)]. With this latter choice for the symmetry coordinates the $\boldsymbol{G}$ matrix will be independent of ρ.

Table 15-5

Symmetry coordinates of CH_3NO_2 that do not involve the torsional angle[a]

$A_1{}'$	$S_1 =$	$(\Delta r_1 + \Delta r_2 + \Delta r_3)/\sqrt{3}$
	$S_2 =$	Δr_{CN}
	$S_3 =$	$(\Delta r_4 + \Delta r_5)/\sqrt{2}$
	$S_4 =$	$(\Delta \alpha_4 + \Delta \alpha_5)/\sqrt{2}$
	$S_5 =$	$(\Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha_3)/\sqrt{3}$
$A_1{}''$	$S_6 =$	$(\Delta r_4 - \Delta r_5)/\sqrt{2}$
	$S_7 =$	$(\Delta \alpha_4 - \Delta \alpha_5)/\sqrt{2}$
$A_2{}''$	$S_9 =$	$\Delta\lambda$ (out-of-plane NO_2 wag)
E'	$S_{10a} =$	$(2\Delta r_1 - \Delta r_2 - \Delta r_3)/\sqrt{6}, S_{10b} = (\Delta r_2 - \Delta r_3)/\sqrt{2}$
	$S_{11a} =$	$(2\Delta\beta_{23} - \Delta\beta_{13} - \Delta\beta_{12})/\sqrt{6}, S_{11b} = (\Delta\beta_{13} - \Delta\beta_{12})/\sqrt{2}$
	$S_{12a} =$	$(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)/\sqrt{6}, S_{12b} = (\Delta\alpha_2 - \Delta\alpha_3)/\sqrt{2}$

[a] The bond and angle coordinates are defined in Fig. 15-6. ν_8 is the torsion.

For dimethylacetylene very detailed theoretical and experimental studies have been undertaken of the problems associated with interpreting its infrared and Raman spectra, and these will be introduced below. Very similar considerations will be required to interpret fully the rotation-contortion-vibration spectrum of nitromethane, and of similar molecules such as methanol and acetaldehyde.

We use the normal coordinate representation of Eq. (15-65), together with the rotational and torsional species of Tables 15-2 and 15-3, in order to give a zero order discussion of the selection rules. The actual analysis of vibrational spectra will require careful determination of the effects of the ρ dependence of the $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices. In the infrared spectrum a transition can occur if the states satisfy the symmetry requirement

$$\Gamma'_{\mathrm{rtv}} \otimes \Gamma''_{\mathrm{rtv}} \supset \Gamma^{*} = A_2'. \tag{15-66}$$

The five A_1' fundamentals are infrared active with accompanying rotational-torsional transitions satisfying

$$\Gamma'_{\mathrm{rt}} \otimes \Gamma''_{\mathrm{rt}} \supset A_2' \tag{15-67}$$

and, from Tables 15-2 and 15-3, the most intense of the rotational-torsional transitions satisfy the selection rules

$$\Delta K_i = 0, \qquad \Delta K_a = 0, \qquad \Delta K_c = \pm 1. \tag{15-68}$$

The five A_1'' fundamentals are infrared active with accompanying rotational-torsional transitions satisfying

$$\Gamma'_{\mathrm{rt}} \otimes \Gamma''_{\mathrm{rt}} \supset A_2'' \tag{15-69}$$

for which the most intense transitions satisfy

$$\Delta K_i = 0, \qquad \Delta K_a = \pm 1, \qquad \Delta K_c = \pm 1. \tag{15-70}$$

For the four A_2'' fundamentals the infrared selection rules from

$$\Gamma'_{\mathrm{rt}} \otimes \Gamma''_{\mathrm{rt}} \supset A_1'' \tag{15-71}$$

are, for the most intense transitions,

$$\Delta K_i = 0, \qquad \Delta K_a = \pm 1, \qquad \Delta K_c = 0. \tag{15-72}$$

The CH_3NO_2 and CH_3BF_2 molecules to which all these results apply are near oblate tops so that K_c, but not K_a, is a useful near quantum number. As a result of asymmetric top effects forbidden transitions with $\Delta K_a = \pm 2$ will occur in the A_1' fundamentals, and with $\Delta K_a = \pm 3$ will occur in the A_1'' and A_2'' fundamentals. Torsional transitions with $\Delta K_i = 6n \pm 3$ and $\Delta K_i = 6n \pm 6$ are allowed by symmetry in these bands, but these will be very weak since they depend on rather high terms in the expansion of $\mu_\alpha^{(r)}(e'', e''; \rho)$ in ρ [see Eq. (15-28)].

Hazra, Ghosh and Kshirsagar (1994) have measured and analyzed the K_i (called m) = 0 subbands in the ν_2 A_1' CN stretching fundamental band at 917.5 cm^{-1}. An asymmetric top Hamiltonian including quartic centrifugal distortion was used in the analysis; it would be interesting to analyze a high resolution spectrum of the $K_i \neq 0$ subbands.

Absorption spectra of the methyl CH stretching overtone bands of CH_3NO_2 with Δv_{CH} = 1-6 have been recorded by Cavagnat and Lespade (1997). The spectra show that at high energy the vibrational contribution to the effective internal rotation potential induces a relative localization of the CH stretching vibrational energy. This study also illustrates how weak interactions between the methyl group and the molecular moiety to which it is attached can have some important consequences for internal vibrational redistribution (IVR) [see the Bibliographical Notes to Chapter 14 on page 474].

The ethyl radical (C_2H_5) has the same MS group as nitromethane, and it has recently become the subject of high resolution spectroscopic study [see Sears, Johnson, Jin and Oatis (1996) and Sørensen (1996)].

15.4.3 Toluene

Toluene $CH_3C_6H_5$ has the same MS group as nitromethane CH_3NO_2, and thus many of the results obtained above apply to it.

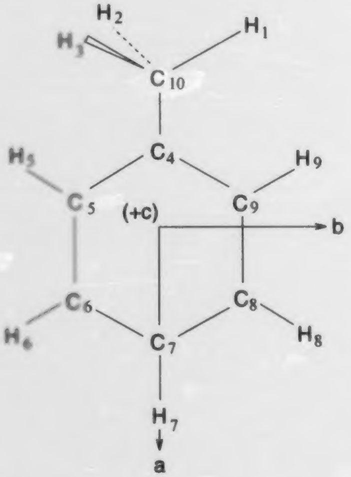


Fig. 15-9. The nuclear numbering convention and the location of the *abc* inertial axes for the toluene molecule.

Figure 15-9 gives the nuclear numbering convention and the *abc* axis locations for the toluene molecule. Just as for nitromethane we number the protons in the methyl group 1, 2 and 3. The MS group G_{12} for toluene is given in Table A-24, where the operation (45) has to be replaced by the operation

(59)(68) which permutes the two pairs of symmetrically located CH nuclei. The sixfold torsional barrier in the ground electronic state (the S_0 state) has been determined to be 4.9 cm^{-1} in $CH_3C_6H_5$ (toluene-d_0) and 4.1 cm^{-1} in $CD_3C_6H_5$ (toluene-d_3) from an analysis of microwave spectra [see Table X in Kreiner, Rudolph and Tan (1973)]. The torsional barrier in the first excited singlet electronic state (the S_1 state) has been estimated as 25 cm^{-1} in toluene-d_0 [Breen, Warren, Bernstein, and Seeman (1987)]. One point of interest in studies of the spectrum of toluene is the appearance of forbidden torsional bands in the $S_1 - S_0$ electronic band system, and we will discuss this in detail. It serves as an example of how the optical selection rules become modified when a molecule is nonrigid. We will also discuss the symmetry of the *effective* torsional potential function of unsymmetrical isotopomers of toluene at the end of this subsection.

Murakami, Ito and Kaya (1981) were the first to observe forbidden torsional bands in the $S_1 - S_0$ electronic band system of toluene. They have also been studied by Breen, Warren and Bernstein (1987), Walker, Richard, Lu, Sibert and Weisshaar (1995), and Siebrand, Zgierski, Zerbetto, Wójcik, Boczar, Chakraborty, Kofron and Lim (1997). The rotational and torsional selection rules for these forbidden bands can be understood using some of the symmetry results discussed above for nitromethane, and a consideration of the dependence of the electronic transition moment on the torsional angle.

In order to determine the torsional and rotational selection rules for allowed transitions in the $S_1 - S_0$ electronic band system of toluene we apply the general analysis presented above in Eqs. (15-23)-(15-32). The selection rules that we require are obtained by considering the conditions under which the following is true [from Eq. (15-24)]

$$\langle \Phi'_{\rm rot}\Phi'_{\rm tor}\Phi'_{\rm vib}\Phi^{(S_1)}_{\rm elec}|\mu^{(1,0)}_{s}|\Phi''_{\rm rot}\Phi''_{\rm tor}\Phi''_{\rm vib}\Phi^{(S_0)}_{\rm elec}\rangle \neq 0, \tag{15-73}$$

where the $\Phi_{\rm tor}$ are torsional wavefunctions [the $\Phi^{(\pm)}_{\rm tor}$ of Eq. (15-49)]. Expressing the space fixed component $\mu^{(1,0)}_{s} = \mu_\zeta$ of the dipole moment operator in terms of the molecule fixed abc components μ_α [see Eqs. (14-12)] and separating the rotational and vibronic integrals we can rewrite this condition as

$$\sum_{\alpha=abc} \langle \Phi'_{\rm rot}|\lambda_{\alpha\zeta}|\Phi''_{\rm rot}\rangle\langle \Phi'_{\rm tor}\Phi'_{\rm vib}\Phi^{(S_1)}_{\rm elec}|\mu_\alpha|\Phi''_{\rm tor}\Phi''_{\rm vib}\Phi^{(S_0)}_{\rm elec}\rangle \neq 0. \tag{15-74}$$

The vibronic matrix element determining the line strength is obtained as [see Eq. (15-25)]

$$\begin{aligned}&\langle \Phi'_{\rm tor}\Phi'_{\rm vib}\Phi^{(S_1)}_{\rm elec}|\mu_\alpha|\Phi''_{\rm tor}\Phi''_{\rm vib}\Phi^{(S_0)}_{\rm elec}\rangle\\ &\qquad = \langle \Phi'_{\rm tor}\Phi'_{\rm vib}|\mu_\alpha(S_1,S_0)|\Phi''_{\rm tor}\Phi''_{\rm vib}\rangle,\end{aligned} \tag{15-75}$$

where $\mu_\alpha(S_1,S_0)$ is the electronic transition moment $\langle \Phi^{(S_1)}_{\rm elec}|\mu_\alpha|\Phi^{(S_0)}_{\rm elec}\rangle$, and we use Eq. (15-28) to expand it as

$$\mu_\alpha(\mathrm{S}_1,\mathrm{S}_0) = \mu_\alpha^{(0)}(\mathrm{S}_1,\mathrm{S}_0;\rho) + \sum_r \mu_\alpha^{(r)}(\mathrm{S}_1,\mathrm{S}_0;\rho)Q_r + \frac{1}{2}\sum_{r,s} \mu_\alpha^{(r,s)}(\mathrm{S}_1,\mathrm{S}_0;\rho)Q_rQ_s + \cdots , \qquad (15\text{-}76)$$

where r and $s = 1$ to 38 for toluene. We neglect the dependence of the electronic transition moment on the 38 small amplitude vibrations but do not neglect its dependence on the torsional angle ρ so that the condition given by Eq. (15-74) becomes

$$\sum_{\alpha=abc} \langle\Phi'_{\mathrm{rot}}|\lambda_{\alpha\zeta}|\Phi''_{\mathrm{rot}}\rangle\langle\Phi'_{\mathrm{tor}}|\mu_\alpha^{(0)}(\mathrm{S}_1,\mathrm{S}_0;\rho)\langle\Phi'_{\mathrm{vib}}|\Phi''_{\mathrm{vib}}\rangle|\Phi''_{\mathrm{tor}}\rangle \neq 0. \qquad (15\text{-}77)$$

This is the equation to be used for determining the selection rules for the $\mathrm{S}_1 - \mathrm{S}_0$ electronic transition in toluene.

The dipole moment components μ_a, μ_b and μ_c have symmetries A_1', A_1'' and A_2'' respectively (see Table A-24), and to proceed further we need the symmetries of the S_0 and S_1 electronic states in $\boldsymbol{G}_{12}$. This is an electronic transition in the benzene ring of toluene and we can make the following identities of the elements of $\boldsymbol{G}_{12}$ with the elements of the $\boldsymbol{D}_{6\mathrm{h}}$ point group as regards the effect of the $\boldsymbol{G}_{12}$ elements on the vibronic variables in the benzene moiety:

$$\{E, (123), (23)^*, (45)(67), (123)(45)(67), (23)(45)(67)^*\} \rightarrow \{E, E, \sigma_\mathrm{h}, C_2, C_2, \sigma_\mathrm{v}\}. \qquad (15\text{-}78)$$

The $\tilde{X}\,{}^1A_{1\mathrm{g}}$ state of benzene correlates with the S_0 state of toluene, and the $\tilde{A}\,{}^1B_{2\mathrm{u}}$ state of benzene correlates with the S_1 state of toluene. Correlating species we obtain the species of the S_0 and S_1 states of toluene as A_1' and A_1'' respectively. From these results we see that $\mu_\alpha^{(0)}(\mathrm{S}_1,\mathrm{S}_0;\rho)$ has symmetry A_1'', A_1' and A_2' as α is a, b or c. The results in Table 15-3 show that $\cos(6n+3)\rho$ transforms as A_1'', $\cos 6n\rho$ transforms as A_1', and $\sin(6n+6)\rho$ transforms as A_2' (where n is a nonnegative integer). Thus we can write [see Eq. (6) of Walker, Richard, Lu, Sibert and Weisshaar (1995)]

$$\mu_a^{(0)}(\mathrm{S}_1,\mathrm{S}_0;\rho) = M_3^a \cos 3\rho + M_9^a \cos 9\rho + \ldots , \qquad (15\text{-}79)$$

$$\mu_b^{(0)}(\mathrm{S}_1,\mathrm{S}_0;\rho) = M_0^b + M_6^b \cos 6\rho + M_{12}^b \cos 12\rho + \ldots , \qquad (15\text{-}80)$$

and

$$\mu_c^{(0)}(\mathrm{S}_1,\mathrm{S}_0;\rho) = M_6^c \sin 6\rho + M_{12}^c \sin 12\rho + \ldots , \qquad (15\text{-}81)$$

where the M_n^α are expansion constants that could be determined, for example, by *ab initio* calculation of the three $\mu_\alpha^{(0)}(\mathrm{S}_1,\mathrm{S}_0;\rho)$ at several ρ values. Note that because of the transformation properties of ρ none of the $\mu_\alpha^{(0)}(\mathrm{S}_1,\mathrm{S}_0;\rho)$ has to vanish. However, if the dependence on the torsional angle ρ were neglected (as one would do if one were to implement the approximation, appropriate for a rigid molecule, of neglecting the dependence of the electronic transition moment on all the nuclear coordinates) then only $\mu_b^{(0)}(S_1, S_0)$ would be nonvanishing. In this 'rigid molecule' approximation the only vibrational transitions that would occur would be those between vibrational states of the same symmetry [see Eq. (14-53)] and this would result in the torsional selection rule $\Delta K_i = 0$, 6, 12, ... [transitions between (+) and (−) components being forbidden; see Eq. (15-49) and Table 15-3]; such bands would have *b* type rotational structure [see Eq. (14-83)]. Allowing for the dependence of $\mu_\alpha(S_1, S_0)$ on ρ means that in addition there can be vibrational bands with $\Delta K_i = 3, 9, \ldots$ $[(+) \leftrightarrow (+)$ and $(-) \leftrightarrow (-)]$ having *a* type rotational structure, and bands with $\Delta K_i = 6$, 12, ... $[(+) \leftrightarrow (-)]$ having *c* type rotational structure. One can expect that the most significant M_n^α in Eqs. (15-79)-(15-81) will be M_0^b and M_3^a, and this is what is found experimentally.

Toluene provides a good example for discussing the effective torsional potential energy function that occurs in the effective rotation-torsion Hamiltonian [see Eq. (15-16)]. Analytical expressions for the effective inverse inertia tensor elements and effective bending potential of a triatomic molecule are given in Eqs. (5.25) and (5.29) of Jensen (1983a) as part of the expression for the nonrigid bender Hamiltonian. These correction terms are obtained as power series in $[v_r+(1/2)]$. Making such an analytical development of the effective rotation-torsion Hamiltonian for toluene is hardly realistic. However, Siebrand, Zgierski, Zerbetto, Wójcik, Boczar, Chakraborty, Kofron and Lim (1997) show an important qualitative result from using the effective torsional potential $V_{\rm eff}(\rho)$, rather than the Born-Oppenheimer potential $V_0(\rho)$, in unsymmetrical isotopomers.

If we presume that the $3N - 7 = 38$ ordinary vibrations in toluene are harmonic, and ignore Coriolis coupling corrections, then the effective torsional potential can be written (in cm^{-1}) as

$$V_{\rm eff}(\rho) = V_0(\rho) + \sum_{r=1}^{38} [v_r + (1/2)]\omega_r(\rho), \tag{15-82}$$

where the 38 harmonic frequencies $\omega_r(\rho)$ are all, in principle, functions of the torsional angle ρ. In the ground state of the 38 ordinary vibrations (i.e., all $v_r = 0$) the effective torsional potential in this approximation is simply the sum of $V_0(\rho)$ and the zero point energy $\sum[\omega_r(\rho)/2]$. The zero point energy is ρ dependent and isotope dependent. This effective potential is the potential that the molecule feels as it internally rotates while the other 38 vibrations are undergoing their zero point vibrations. Since the zero point energy can change as ρ changes the effective potential can be noticeably different from the Born-Oppenheimer potential. In any fitting of experimental torsional energy levels for a single isotopomer it is the effective potential for that isotopomer that will be determined.

For toluene-d_0 and toluene-d_3 the MS group is $\boldsymbol{G}_{12}$ and $V_{\rm eff}(\rho)$ has to be totally symmetric in that group. The most general expansion of $V_{\rm eff}(\rho)$ is as given in Eq. (15-50) and, as in nitromethane, the only nonvanishing terms (i.e., terms of symmetry A_1' in $\boldsymbol{G}_{12}$) are the $\cos n\rho$ terms having $n = 6, 12, 18, \ldots$. The V_6 term is sufficient to fit the data for toluene-d_0 or toluene-d_3, giving experimentally determined effective torsional barriers of 4.9 cm^{-1} for d_0, and 4.1 cm^{-1} for d_3 (see above). For toluene-d_1 and toluene-d_2 (having one and two of the protons in the CH$_3$ group replaced by a deuteron, respectively) the MS group is $\boldsymbol{G}_4 = \{E,(45)(67),(12)^*,(12)(45)(67)^*\}$ where the 1 and 2 label the two protons in the methyl group for toluene-d_1 and the two deuterons in toluene-d_2. The Born-Oppenheimer potential V_0 is, by definition, isotopically invariant and therefore totally symmetric in $\boldsymbol{G}_{12}$, but the zero-point energy only has to be symmetric in $\boldsymbol{G}_4$ for these two isotopomers. This means that in general $V_{\mathrm{eff}}(\rho)$ only has $\boldsymbol{G}_4$ symmetry for these isotopomers, and therefore terms in $\cos n\rho$ with $n = 2, 4, 6, 8 \ldots$ can be nonvanishing. Experimental results and *ab initio* calculations support this conclusion. In the d_1 and d_2 molecules V_2^{eff} has opposite sign and a magnitude of about 20 cm^{-1}; the $V_4^{(\mathrm{eff})}$ constants are close to zero for both molecules [see Siebrand, Zgierski, Zerbetto, Wójcik, Boczar, Chakraborty, Kofron and Lim (1997)].

15.4.4 Ethane and dimethylacetylene

The ethane and dimethylacetylene molecules have been of great spectroscopic interest for more than 60 years because of their internal rotation and high symmetry. Before the work of Kemp and Pitzer (1936) it was thought that there was essentially free internal rotation about single bonds such as that which occurs between the two CH$_3$ groups in ethane [see for example Eyring (1932)]. Kemp and Pitzer (1936), in their historic statistical mechanics paper on ethane, show that a high torsional barrier of about 1000 cm^{-1} is required to explain the results of experiments on the entropy and specific heat. As far as spectroscopists are concerned it is unfortunate that the paper by Howard (1937), who shows that a study of the rotation-vibration spectrum of ethane also leads one to conclude that there is a high torsional barrier, was submitted for publication after that of Kemp and Pitzer (1936).[7] The most precise determination of the torsional barrier in C$_2$H$_6$ ethane (1012.5 cm^{-1}) is from a high resolution infrared study by Moazzen-Ahmadi, McKellar, Johns and Ozier (1992). The most precise determination of the torsional barrier in C$_4$H$_6$ dimethylacetylene (6.0 cm^{-1}) is from high resolution infrared studies by Plíva, Pine and Civiš (1996) and di Lauro, Bunker, Johns and McKellar (1997). Nakagawa, Hayashi, Endo, Saito and Hirota (1984) have determined the torsional barrier in CH$_3$CCCD$_3$ to be 5.6 cm^{-1} using microwave spectroscopy.

However, there is much more to the study of ethane and dimethylacetylene than the determination of the torsional barriers, and the determination of the barriers is far from straightforward. The molecules have very interesting dynamics and unusual symmetry properties; Longuet-Higgins (1963) introduced the MS group $\boldsymbol{G}_{36}$ for them, after which Hougen (1964a) showed that it is necessary to introduce an extended molecular symmetry (EMS) group, or double group, which we denote here as $\boldsymbol{G}_{36}$(EM) in order to make full use of symmetry in their study. Dimethylacetylene was the first nonrigid molecule for which the nonuniqueness of the symmetry species of the normal coordinates was pointed out [Hougen (1965)], and for which quantitative calculations of the effect of the ρ dependence of the $\boldsymbol{F}$ matrix on the normal coordinates were carried out [Bunker and Hougen (1967)]. Hougen (1980b), in a discussion of the perturbations that can occur between the rotation-torsion-vibration energy levels of ethane when internal rotation tunneling is allowed for, relates the results obtained using the $\boldsymbol{D}_{3\mathrm{d}}$ and $\boldsymbol{G}_{36}$(EM) groups, and points out that when ethane undergoes internal rotation its center of symmetry is destroyed and rotation-vibration levels of g and u symmetry in $\boldsymbol{D}_{3\mathrm{d}}$ can perturb each other. The 'torsional splittings' in degenerate vibrational states of ethane are discussed by di Lauro, Lattanzi and Nivellini (1997) (see also references therein); such splittings depend significantly on the extent of torsional Coriolis coupling. Bunker, Johns, McKellar and di Lauro (1993) (and references therein) and Bunker and di Lauro (1995) discuss the problems involved in analyzing the infrared and Raman perpendicular bands of dimethylacetylene in order to determine the barrier. In this work a detailed study of the normal modes, and an analysis of the infrared and Raman selection rules, are made.

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[7] In fact, as the late Prof. E. B. Wilson told PRB many years ago in a conversation at an Ohio State University internalal Symposium on Molecular Spectroscopy, J. B. Howard had obtained his result sometime earlier. Prof. Wilson, to his great regret, caused a delay in the publication of Howard's paper because he found the first draft obscure and recommended that it be reworked.

Except in ultra high resolution spectroscopic studies ethane can be considered to be a rigid molecule and the possibility of torsional tunneling can be neglected. The lack of coincidences between the infrared active (u) and Raman active (g) fundamentals shows that the equilibrium structure of ethane is centrosymmetric (staggered) of $\boldsymbol{D}_{3\mathrm{d}}$ point group symmetry (see Section 14.3). The ν_4 $A_{1\mathrm{u}}$ torsional fundamental band in ethane is forbidden in the infrared in absorption, but it can steal intensity from the allowed infrared active fundamental bands by rotation-vibration interaction. Moazzen-Ahmadi, Gush, Halpern, Jagannath, Leung and Ozier (1988) have measured the forbidden torsional fundamental $v_4 = 1 \leftarrow 0$, and forbidden hot band $v_4 = 2 \leftarrow 1$ of ethane in the 225 to 340 cm^{-1} region of the infrared spectrum at high resolution; Fig. 1 of that paper gives a relevant energy level diagram. In a high barrier molecule such as ethane the determination of the $v = 0$, 1 and 2 torsional energies allows one to determine the torsional barrier height by adjusting the parameters of the torsional potential function in a fitting of the torsional eigenvalues to the experimental torsional energies. In this way, and including data involving the ν_9 fundamental and $\nu_9+\nu_4-\nu_4$ hot band, a barrier of 1012.5 cm^{-1} was determined for C_2H_6 ethane by Moazzen-Ahmadi, McKellar, Johns and Ozier (1992), who also give references to earlier theoretical and experimental work. More recent studies are concerned with the Raman spectra of ethane and its deuterated isotopomers [see Fernández-Sánchez, Gómez, and Montero (1993) and the references therein].

A very important feature of the symmetry of the ethane and dimethylacetylene molecules is the need to use an extended molecular symmetry (EMS) group. We discuss how this group arises and we use the dimethylacetylene molecule as the example.

The dimethylacetylene molecule in its reference configuration is shown in Fig. 15-10. The molecule has a very low barrier to internal rotation, and its MS group is the group $\boldsymbol{G}_{36}$. The MS group of acetone is isomorphic to that of dimethylacetylene, and its character table is given in Table A-28. The transformation properties of the $\hat{J}_a, \mu_a, \alpha_{ab}$, etc., given in Table A-28 apply to acetone but not to dimethylacetylene. The species of Γ^* is A_3.

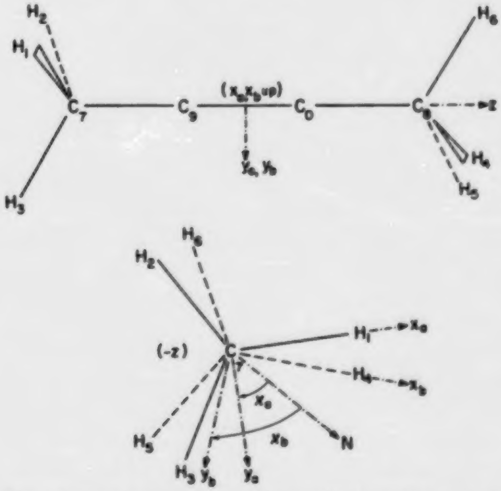

Fig. 15-10. The reference configuration of dimethylacetylene and the definition of the rotor fixed axes (x_a, y_a, z) and (x_b, y_b, z). These axes have origin at the nuclear center of mass O and the x_a and x_b axes are in the $H_1C_7C_8$ and $H_4C_8C_7$ planes, respectively. ON is the node line from which the Euler angles χ_a and χ_b are measured (see Fig. 10-1).

The molecule fixed z axis of the reference configuration is defined as pointing from C_7 to C_8, and its orientation in space is given by the Euler angles θ and ϕ. We introduce x_ay_a and x_by_b axes that rotate with the $C_7(H_1H_2H_3)$ and $C_8(H_4H_5H_6)$ rotors, respectively; x_a being in the $H_1C_7C_8$ plane and x_b being in the $H_4C_8C_7$ plane as indicated in Fig. 15-10. The orientation of these axes is defined by the two Euler angles χ_a and χ_b. Assuming no torsional barrier the zero order rotational-torsional Hamiltonian is (in cm^{-1})

$$[B(\hat{J}_x{}^2 + \hat{J}_y{}^2) + A_{\text{top}}(\hat{J}_{za}^2 + \hat{J}_{zb}^2)]\hbar^{-2}, \tag{15-83}$$

where A_{top} is the rotational constant for a CH_3 group, and $\hat{J}_{za}$ and $\hat{J}_{zb}$ are the z components of the angular momenta of each CH_3 group. The zero order rotational-torsional wavefunctions are

$$\Phi_{\mathrm{rt}} = [(1/(2\pi))]S_{Jkm}(\theta,\phi)\exp(ik_a\chi_a)\exp(ik_b\chi_b), \tag{15-84}$$

where k, k_a, and k_b are positive or negative integers, and $k = k_a + k_b$. The function $S_{Jkm}(\theta,\phi)$ is introduced in Eq. (11-16). The transformation properties of θ, ϕ, χ_a, and χ_b under the effect of the generating operations of $\boldsymbol{G}_{36}$ are given in Table 15-6; from these results the effect of any operation of $\boldsymbol{G}_{36}$ on the angles can be deduced. The symmetry classification of the rotational-torsional wavefunctions can be determined from the results in Table 15-6, and the results are given in Table 15-7.

Table 15-6

The transformation properties of the Euler angles of dimethylacetylene under the effect of the generating operations of G_{36}

E	(123)	(456)	(23)(56)*	(14)(26)(35)(78)(90)*
θ	θ	θ	$\pi - \theta$	θ
ϕ	ϕ	ϕ	$\phi + \pi$	ϕ
χ_a	$\chi_a + 2\pi/3$	χ_a	$\pi - \chi_a$	$\chi_b + \pi$
χ_b	χ_b	$\chi_b - 2\pi/3$	$\pi - \chi_b$	$\chi_a + \pi$

Table 15-7

The symmetry classification of the rotational-torsional functions of dimethylacetylene in G_{36}[a]

	$\lvert k_a + k_b\rvert$		
$\lvert k_a - k_b\rvert$	0	$3n \pm 1$	$3n \pm 3$
0:	$A_1(J \text{ even})$ $A_2(J \text{ odd})$	E_1	$A_1 \oplus A_2$
$3m \pm 1$:	E_3	G	$E_3 \oplus E_4$
$3m \pm 3$:	$A_1 \oplus A_3(J \text{ even})$ $A_2 \oplus A_4(J \text{ odd})$	$E_1 \oplus E_2$	$A_1 \oplus A_2 \oplus A_3 \oplus A_4$

[a] n and m are nonnegative integers.

In the above there has been no attempt made to separate rotation from torsion. However, a detailed understanding of the spectrum and energy levels of this molecule requires that we introduce a torsional barrier and ρ dependent force constants. To do this we must use a zero order wavefunction that is separable into rotational, torsional, and vibrational parts. We do this by introducing the rotational and torsional angles

$$\chi = (\chi_a + \chi_b)/2, \qquad \gamma = (\chi_a - \chi_b)/2, \tag{15-85}$$

where these angles are defined mod 2π. The torsional (dihedral) angle $\tau = (\chi_a - \chi_b) = 2\gamma$. The zero order rotation-torsion Hamiltonian (in cm^{-1}) becomes

$$[B(\hat{J}_x{}^2 + \hat{J}_y{}^2) + A(\hat{J}_z^2 + \hat{J}_\gamma^2)]\hbar^{-2}, \tag{15-86}$$

where $A = A_{\rm top}/2$ is the rotational constant for the whole molecule. The rotational wavefunctions will involve the three Euler angles θ, ϕ, and χ upon which the intramolecular potential function does not depend. The zero order wavefunctions are

$$\Phi_{\rm rtv} = [1/(2\pi)]S_{Jkm}(\theta,\phi)\exp(ik\chi)\exp(ik_i\gamma)\Phi_{\rm vib}[Q_s(\gamma)], \tag{15-87}$$

and the 23 normal coordinates $Q_s(\gamma)$ are allowed to depend parametrically on the torsional angle γ. The Hamiltonian and zero order wavefunctions are now written in terms of IAM, rather than PAM, coordinates.

We wish to classify the rotational, torsional, and vibrational wavefunctions separately where these functions are

$$\begin{aligned} \Phi_{\rm rot} &= [1/(2\pi)]^{1/2}S_{Jkm}(\theta,\phi)\exp(ik\chi), \\ \Phi_{\rm tor} &= [1/(2\pi)]^{1/2}\exp(ik_i\gamma), \\ \Phi_{\rm vib} &= \Phi_{\rm vib}[Q_s(\gamma)]. \end{aligned} \tag{15-88}$$

Once we have achieved this we can determine selection rules on K and K_i for vibrational transitions. However, to make the separate classification of $\Phi_{\rm rot}, \Phi_{\rm tor}$, and $\Phi_{\rm vib}$ in G_{36} we run into a difficulty of *double valuedness* as was first pointed out by Hougen (1964a). For example,

$$(123)\chi = (123)[(\chi_a + \chi_b)/2] \tag{15-89}$$

and if we use the transformation properties of χ_a, and χ_b given in Table 15-6 we obtain

$$(123)\chi = \chi + (\pi/3). \tag{15-90}$$

However, if we replace χ_a by $\chi_a+2\pi$ (or χ_b by $\chi_b+2\pi$) in Eq. (15-89), which does nothing to the coordinates of the nuclei and electrons in space, we obtain

$$(123)\chi = \chi + (4\pi/3). \tag{15-91}$$

An exactly similar result is obtained for the transformation properties of γ. Because of this ambiguity in the transformation properties of χ and γ we cannot classify $\Phi_{\rm rot}$ having an odd value of k, or $\Phi_{\rm tor}$ having an odd value of k_i, unambiguously in the group $\boldsymbol{G}_{36}$. For example, the character generated by $\Phi_{\rm rot}$ under (123) is $+\exp(i\pi k/3)$ using Eq. (15-90), but it is $\exp(4i\pi k/3) = -\exp(i\pi k/3)$ using Eq. (15-91) if k is odd. The same kind of thing happens for $\Phi_{\rm tor}$ and for some $\Phi_{\rm vib}$, and this happens for all elements of $\boldsymbol{G}_{36}$ (including E).

One might think that this means that there is something wrong with the elements of $\boldsymbol{G}_{36}$. This is not the case and there is no difficulty classifying the rotation-torsion-vibration wavefunction in $\boldsymbol{G}_{36}$. For example, in the vibrational ground state $\Phi_{\rm vib}$ has species A_1 in G_{36} and k and k_i have the same parity. This means that when k is odd then k_i is also odd and the character generated by the product function $\Phi_{\rm rot}\Phi_{\rm tor}$ is unambiguous. This is because $\Phi_{\rm rot}$ and $\Phi_{\rm tor}$ have canceling ambiguities. This problem of double valuedness arises because we want to classify the wavefunctions $\Phi_{\rm rot}$, $\Phi_{\rm tor}$ and $\Phi_{\rm vib}$ separately. This is a good idea but it involves defining the angles χ and γ, and these coordinates are rather peculiar. Any configuration of the molecule in space is defined by two sets of these coordinates; the configurations represented by the coordinates (χ,γ) and $(\chi+\pi,\gamma+\pi)$ are identical. Although these coordinates lead to a useful expression for the Hamiltonian and wavefunctions they have this unfortunate ambiguity as to their values. In order to deal with this we have to pretend that the configurations described by the angles (χ,γ) and $(\chi+\pi,\gamma+\pi)$ are not the same. We achieve this by introducing the special symmetry operation E' (which we consider to be different from the identity E), and by defining four generating operations a, b, c and d as transforming χ and γ unambiguously. The operation E' is defined as an operation that increases both χ and γ by π (this is equivalent to changing χ_a or χ_b by 2π, and it does not affect the space fixed coordinates; it is the identity operation for the overall rotation-torsion-vibration wavefunction). We introduce the operations a, b, c and d which have the same effect on the space fixed coordinates as the $\boldsymbol{G}_{36}$ operations (123), (456), (14)(26)(35)(78)(90)* and (23)(56)* respectively but which we *define* to have the single valued effect on the Euler angles χ and γ as given[8] in Table 15-8. The group generated by these five operations is twice the size of the MS group $\boldsymbol{G}_{36}$ and it is called a double group or an extended molecular symmetry (EMS) group; we denote[9] it $\boldsymbol{G}_{36}$(EM). The character table of $\boldsymbol{G}_{36}$(EM) is given in Table A-33. The irreducible representations having the same character under E' as under E constitute the (single valued) irreducible representations of $\boldsymbol{G}_{36}$ and we add an extra subscript label 's'. The irreducible representations having characters of opposite sign under E' and E constitute double valued representations of $\boldsymbol{G}_{36}$ and are labeled with a 'd' subscript. The overall wavefunction cannot belong to a d representation (since the group $\boldsymbol{G}_{36}$ is perfectly fine for the classification of such 'real' states), but the individual (artificial) basis wavefunctions $\Phi_{\rm rot}$, $\Phi_{\rm tor}$ and $\Phi_{\rm vib}$ can.

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[8] Note that Table 1 of Bunker and di Lauro (1995) has some misprints.

[9] It is sometimes called $G_{36}^{\dagger}$ or $G_{36}^{(2)}$.

Table 15-8

The transformation properties of θ, ϕ, χ and γ for dimethylacetylene under the effect of the generating operations of G_{36}(EM)[a]

E	a	b	d	c	E'
θ	θ	θ	$\pi-\theta$	θ	θ
ϕ	ϕ	ϕ	$\phi+\pi$	ϕ	ϕ
χ	$\chi+\pi/3$	$\chi-\pi/3$	$\pi-\chi$	$\chi+\pi$	$\chi+\pi$
γ	$\gamma+\pi/3$	$\gamma+\pi/3$	$-\gamma$	$-\gamma$	$\gamma+\pi$

[a] ϕ, χ, and γ are mod 2π and $0 \le \theta \le \pi$.

Table 15-9

The separate classification of the rotational[a] and torsional[b] wavefunctions of dimethylacetylene in G_{36}(EM)

K	Γ_{rot}	K_i	Γ_{tor}
0 (J even)	A_{1s}	0	A_{1s}
(J odd)	A_{2s}		
$6n \pm 1$	E_{2d}	$6m \pm 1$	E_{3d}
$6n \pm 2$	E_{1s}	$6m \pm 2$	E_{3s}
$6n \pm 3$	$A_{3d} \oplus A_{4d}$	$6m \pm 3$	$A_{1d} \oplus A_{3d}$
$6n \pm 6$	$A_{1s} \oplus A_{2s}$	$6m \pm 6$	$A_{1s} \oplus A_{3s}$

[a] n is a nonnegative integer ; $K \ge 0$.
[b] m is a nonnegative integer; $K_i \ge 0$.

In the EMS group G_{36}(EM) the transformation properties of θ, ϕ, χ, and γ are definite and are given in Table 15-8. Notice that $a^3 \equiv b^3 \equiv E'$. We can classify unambiguously all rotational, torsional, and vibrational wavefunctions in the group. The rotational and torsional species are given in Table 15-9. The species of the $3N-7=23$ normal coordinates of dimethylacetylene in G_{36}(EM) are not unique, and as shown by Hougen (1965) the species are given by

$$\Gamma(Q) = 4A_{1s} \oplus 3A_{4s} \oplus (4-n)E_{1d} \oplus (4-n)E_{2d} \oplus nE_{1s} \oplus nE_{2s}, \qquad (15\text{-}92)$$

where n is an integer satisfying

$$0 \le n \le 4. \qquad (15\text{-}93)$$

The degenerate normal coordinates occur in pairs, and an $E_{1d} \oplus E_{2d}$ pair can be converted into an $E_{1s} \oplus E_{2s}$ pair by a suitable change in the γ dependence of the force constants. This is discussed in detail in Bunker (1967).

Further discussion, with application to the spectrum of ethane, is given by Lattanzi, di Lauro and Legay-Sommaire (1992) and di Lauro and Lattanzi (1993). Symmetry coordinates having '$n = 0$ symmetry' in Eq. (15-92) are given in Table 15-10. The selection rules on the fundamentals of these vibrations are given in Table 15-10. In this table the symmetry coordinates numbered 9 though 16 involve vibrational displacements perpendicular to the CCCC skeleton, and it is these vibrations that have the variable symmetry species in $\boldsymbol{G}_{36}$(EM). The E_{1d} vibrations involve perpendicular vibrations in each half of the molecule that are *cis* coupled for all values of γ, and the E_{2d} vibrations are *trans* coupled for all values of γ. One can immediately appreciate intuitively why the E_{1d} vibrations are infrared active and why the E_{2d} vibrations are infrared inactive. Alternatively, the E_{1s} vibrations are *cis* coupled when the molecule is at eclipsed configurations but *trans* coupled at staggered configurations, and the E_{2s} vibrations are *trans* coupled when the molecule is at eclipsed configurations but *cis* coupled at staggered configurations. Lattanzi, di Lauro and Legay-Sommaire (1992) have determined that all three pairs of degenerate vibrations in ethane are of the E_{1d}/E_{2d} type from a detailed study of its infrared spectrum. Ironically, for the only perpendicular fundamentals of dimethylacetylene that have been rotational and torsionally analyzed, the most useful symmetry coordinates do not have E_{1d}/E_{2d} or E_{1s}/E_{2s} symmetry. They have symmetry G_s, and this symmetry cannot arise for the normal coordinates from the diagonalization of the FG matrix. Such coordinates are fourfold degenerate and uncoupled perpendicular vibrations of the ends of the molecule analogous to the coordinates S_9 to S_{11} for nitromethane in Table 15-5.

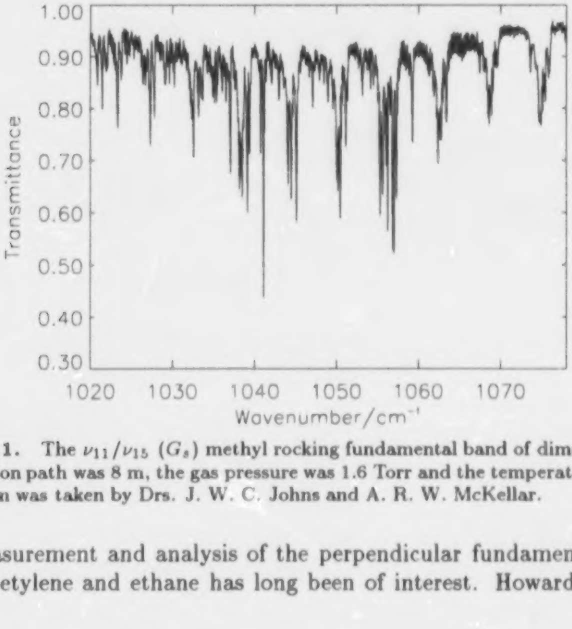

Fig. 15-11. The ν_{11}/ν_{15} (G_s) methyl rocking fundamental band of dimethylacetylene. The absorption path was 8 m, the gas pressure was 1.6 Torr and the temperature was 213 K. The spectrum was taken by Drs. J. W. C. Johns and A. R. W. McKellar.

The measurement and analysis of the perpendicular fundamental bands of dimethylacetylene and ethane has long been of interest. Howard (1937) first

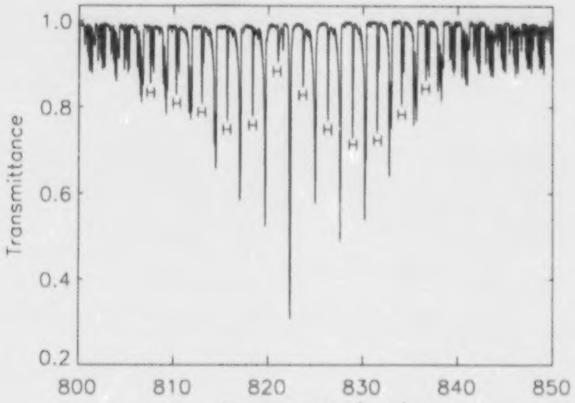

Fig. 15-12. The ν_9 (E_u) methyl rocking fundamental band of ethane. The absorption path was 2 m, the gas pressure was 0.4 Torr and the temperature was 133 K. The hot band $\nu_9+\nu_4-\nu_4$ is marked 'H' (ν_4 is the torsion at 289 cm^{-1}). The spectrum was taken by Drs. J. W. C. Johns and N. Moazzen-Ahmadi.

studied the structure of these bands in ethane, and his theoretical ideas were reconsidered by M. H. L. Pryce [in Mills and Thompson (1954)] for the low barrier molecule dimethylacetylene. It was realized that for the three types of perpendicular methyl group vibration ν_9/ν_{13}, ν_{10}/ν_{14}, and ν_{11}/ν_{15} of dimethylacetylene it was appropriate to use 'end-to-end uncoupled' vibrational coordinates which we would classify as being of G_s symmetry in $\boldsymbol{G}_{36}$(EM). Further developments were made by Kirtman (1964), Bunker and Longuet-Higgins (1964), Hougen (1964a,1965), and Papoušek (1968). Infrared spectra of dimethylacetylene were recorded by Crawford (1939), Mills and Thompson (1954), and Olson and Papoušek (1971). But it was not until the work of Bunker, Johns, McKellar and di Lauro (1993) that the rotational fine structure in a perpendicular band (the ν_{11}/ν_{15} methyl rocking fundamental band) was resolved. This spectrum was taken at a resolution of 0.002 cm^{-1} of a sample cooled to about 213 K, and an overview is shown in Fig. 15-11 from 1000 to 1070 cm^{-1}; here the resolution has been degraded to 0.04 cm^{-1} to make the spectrum clearer. This important experimental breakthrough gave impetus for the development of the theory, and necessary computer codes, so that the spectrum could be fitted and simulated. The theory required to analyze this band is given in Bunker and di Lauro (1995), and this was extended in di Lauro, Bunker, Johns and McKellar (1997) to allow the perturbing E_{2d} band $\nu_4+\nu_{16}$ at 1057 cm^{-1} to be included in the simulation. This lead to a determination of the effective torsional barrier as 6.0 cm^{-1} in the ground vibrational state in agreement with that obtained by Plíva, Pine and Civiš (1996) from their analysis of the ν_{11}/ν_{15} perpendicular CH stretching fundamental band made using the same theory. To show that Howard was clearly correct in his analysis that the structure of the perpendicular fundamentals of ethane show it to be essentially rigid we show a scan of the perpendicular methyl rocking fundamental band of ethane in Fig. 15-12. Comparing this with Fig. 15-11 we see that there are none of the clusters of Q-branches that the low barrier molecule gives.

Table 15-10

The selection rules[a] on the fundamentals of dimethylacetylene using the G_{36}(EM) group

			Selection rules	
No.	Approximate description	Species	Infrared ($\Delta J = 0, \pm 1$)	Raman ($\Delta J = 0, \pm 1, \pm 2$)
1	C–H stretch	A_{1s}	Inactive[a]	$\Delta K = \Delta K_i = 0$
2	C ≡ C stretch			
3	CH$_3$ deformation			
4	C–C stretch			
6	C–H stretch	A_{4s}	$\Delta K = \Delta K_i = 0$	Inactive[a]
7	CH$_3$ deformation			
8	C–C stretch			
9	C–H stretch	E_{1d}	$\Delta K = \pm 1, \Delta K_i = 0$	Inactive[a]
10	CH$_3$ deformation			
11	CH$_3$ rock			
12	Skeletal bend			
13	C–H stretch	E_{2d}	Inactive[a]	$\Delta K = \pm 1, \Delta K_i = 0$
14	CH$_3$ deformation			
15	CH$_3$ rock			
16	Skeletal bend			

[a] Neglecting the very weak transitions with ΔK or ΔK_i larger than one. ν_5 is the torsion.

As mentioned above the fact that ethane has a $\boldsymbol{D}_{3d}$ staggered equilibrium structure, rather than a $\boldsymbol{D}_{3h}$ eclipsed one, was determined by studying both the infrared and Raman spectrum. For dimethylacetylene the determination of its equilibrium structure as being eclipsed or staggered also requires that the infrared and Raman spectra be studied [see Bunker and di Lauro (1995)]. The Raman spectrum of a perpendicular fundamental band of dimethylacetylene has not yet been obtained with enough intensity and resolution to enable this determination to be made [but see Messler, Schrötter and Sarka (1994)]. Thus although the magnitude of the torsional barrier for dimethylacetylene is accurately known its sign is unknown.

15.4.5 Hydrogen peroxide

The equilibrium structure of the hydrogen peroxide molecule is nonplanar and it has point group symmetry C_2. To symmetry label the rotational levels in the event of there being no torsional tunneling one would use the group $C_2(M)$ given in Table A-4. However, torsional tunneling effects are observed in the spectrum and the MS group that one needs to use to allow fully for this tunneling is the MS group G_4 given in Table A-21. As with dimethylacetylene a separate classification of the rotational, torsional and vibrational basis functions requires the use of an extended molecular symmetry group. The character table of the EMS group for hydrogen peroxide, $G_4(EM)$, is given in Table A-31. We will briefly summarize some interesting aspects of the symmetry and spectroscopy of the molecule. For more information the reader should study the theoretical details given in the papers of Dellepiane, Gussoni and Hougen (1973) and Hougen (1984), and the experimental and theoretical analysis given by Flaud, Camy-Peyret, Johns and Carli (1989). In Edition 1 we followed the convention of Dellepiane, Gussoni and Hougen (1973) in labeling the irreducible representations of $G_4(EM)$ in a manner based on C_{2v}, but Hougen (1984) changed to a better notation based on C_{2h}, and so we have done the same in Table A-31.

We follow the same procedure as used for dimethylacetylene to obtain the EMS group from the MS group G_4 given in Table A-21. We label the nuclei $H_1O_3O_4H_2$, and we introduce in the reference configuration the rotor fixed axes (x_1, y_1, z) and (x_2, y_2, z) such that the z axis points from O_3 to O_4, and the x_1 and x_2 axes are in the $H_1O_3O_4$ and $H_2O_4O_3$ planes respectively.[10] We introduce Euler angles (θ, ϕ, χ_1) and (θ, ϕ, χ_2) to give the orientations in space of the rotor fixed axes. The transformation properties of these four Euler angles under the elements of G_4 are given in Table 15-11.

We use a zero order separable rotation-torsion-vibrational wavefunction as given in Eq. (15-87) with $\chi = (\chi_1 + \chi_2)/2$ and $\gamma = (\chi_1 - \chi_2)/2$, respectively. Note that, as in dimethylacetylene, the torsional (dihedral) angle $\tau = \chi_1 - \chi_2$ is given by 2γ, and χ and γ both range from 0 to 2π. To define the elements of the EMS group $G_4(EM)$ we define symmetry operations E', a and b. The operation E' is defined as increasing both χ and γ by π (this is equivalent to changing χ_1 or χ_2 by 2π, and it does not change the space fixed coordinates). The operations a and b transform the space fixed coordinates in the same way as the G_4 operations (12)(34) and E^* respectively, and they are defined as transforming χ and γ according to Table 15-12. With these three operations we can generate all the elements of the group $G_4(EM)$, and we can use Table 15-12 to determine the effect of any element of the group on θ, ϕ, χ and γ. Hougen (1984) calls

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[10] We label the rotors using 1 and 2, rather than a and b as done for dimethylacetylene to avoid the possibility of introducing a rotor quantum number k_a that could be confused with the asymmetric top rotational quantum number.

Table 15-11

The transformation properties of θ, ϕ, χ_1 and χ_2 for hydrogen peroxide under the effect of the operations of G_4 [a]

E	$(12)(34)$	E^*	$(12)(34)^*$
θ	$\pi-\theta$	$\pi-\theta$	θ
ϕ	$\phi+\pi$	$\phi+\pi$	ϕ
χ_1	$\pi-\chi_2$	$-\chi_1$	$\chi_2+\pi$
χ_2	$\pi-\chi_1$	$-\chi_2$	$\chi_1+\pi$

[a] ϕ, χ_1, and χ_2 are mod 2π and $0 \leq \theta \leq \pi$.

a, *b* and E' by the names *c*, *ic*, and *iσ* respectively, and in Dellepiane, Gussoni and Hougen (1973) they are called A, $E'C$ and E' respectively.[11]

Table 15-12

The transformation properties of θ, ϕ, χ and γ for hydrogen peroxide under the effect of the generating operations of G_4(EM)[a]

E	a	b	E'
θ	$\pi-\theta$	$\pi-\theta$	θ
ϕ	$\phi+\pi$	$\phi+\pi$	ϕ
χ	$\pi-\chi$	$\pi-\chi$	$\chi+\pi$
γ	γ	$\pi-\gamma$	$\gamma+\pi$

[a] ϕ, χ, and γ are mod 2π and $0 \leq \theta \leq \pi$.

With the notation used here the operation *ab* in G_4(EM) does not change the Euler angles and so it is appropriate to use this operation as the operation that defines the g and u label of the irreducible representations. All rotational wavefunctions are of g symmetry in G_4(EM). The effect of these operations on the ordinary bond lengths and angles is straightforward to determine, and it is possible to classify rotational, torsional and vibrational basis wavefunctions in the G_4(EM) group [see Tables 2, 3 and 4 in Hougen (1984)].

In hydrogen peroxide there are two distinct torsional barriers: The *cis* barrier at the planar *cis* conformation (for which $\tau = 0$) and the *trans* barrier at the planar *trans* conformation (for which $\tau = \pi$). These barriers are substantial and the *cis* barrier is much higher than the *trans* barrier. Thus, in contrast to dimethylacetylene, a high torsional barrier model is more appropriate in zero order rather than a low barrier model. We can understand the symmetry of the energy levels of this molecule by using a torsional energy level correlation diagram in which we connect the high and zero torsional barrier energy levels maintaining $\boldsymbol{G}_4$(EM) symmetry.

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[11] We have attempted to adopt a consistent notation for the three EMS groups G_4(EM), G_{16}(EM) and G_{36}(EM).

Table 15-13

The $\boldsymbol{C}_2$(M) subgroup of $\boldsymbol{G}_4$(EM), and the reverse-correlation species in $\boldsymbol{G}_4$(EM)

C_2(M):	E	a	:	G_4(EM) species
A:	1	1	:	$A_{gs}\oplus A_{us}\oplus A_{gd}\oplus A_{ud}$
B:	1	-1	:	$B_{gs}\oplus B_{us}\oplus B_{gd}\oplus B_{ud}$

Different subgroups of $\boldsymbol{G}_4$(EM) are appropriate for different torsional barrier situations [see Dellepiane, Gussoni and Hougen (1973)]. If both the *cis* and *trans* barriers are insuperable (when the molecule can be considered as a C_2 molecule) the MS group is $\boldsymbol{C}_2(\text{M}) = \{E,a\}$. If only the *cis* barrier is insuperable (when the molecule can be considered as a C_{2h} molecule) the MS group is $\boldsymbol{C}_{2h}(\text{M}) = \{E,a,ab,b\}$. Finally, if only the *trans* barrier is insuperable (when the molecule can be considered as a C_{2v} molecule) the MS group is $\boldsymbol{C}_{2v}(\text{M}) = \{E,a,E'ab,E'b\}$. The character tables of these groups are given in Tables 15-13, 15-14 and 15-15. The reverse correlations to the irreducible representations of $\boldsymbol{G}_4$(EM) are also given in these three tables.

Table 15-14

The $\boldsymbol{C}_{2h}$(M) subgroup of $\boldsymbol{G}_4$(EM), and the reverse-correlation species in $\boldsymbol{G}_4$(EM)

C_{2h}:	E	a	ab	b	:	G_4(EM) species
A_g:	1	1	1	1	:	$A_{gs}\oplus A_{gd}$
A_u:	1	1	-1	-1	:	$A_{us}\oplus A_{ud}$
B_g:	1	-1	1	-1	:	$B_{gs}\oplus B_{gd}$
B_u:	1	-1	-1	1	:	$B_{us}\oplus B_{ud}$

We now construct the correlation diagram for the torsional energy levels. In the high barrier limit with no observable torsional tunneling effects the

MS group is the $C_2(M)$ group given in Table 15-13. The torsional normal coordinate Q_4 is of symmetry A and thus each torsional energy level, labeled successively $v_4 = 0, 1, 2, \ldots$, is of symmetry A which reverse-correlates with $A_{gs} \oplus A_{gd} \oplus A_{ud} \oplus A_{us}$ in $G_4(EM)$ [Flaud, Camy-Peyret, Johns and Carli (1989) use n instead of v_4]. If there is tunneling through the *trans* barrier, but not through the *cis* barrier, the MS group is the $C_{2h}(M)$ group, and the torsional normal coordinate is of species A_u. Successive torsional states are of symmetry A_g or A_u as the torsional quantum number (which we call v_4^t in this case) is even or odd respectively, and these reverse-correlate with $A_{gs} \oplus A_{gd}$ or $A_{us} \oplus A_{ud}$ respectively in $G_4(EM)$. In the free rotor limit the free rotor torsional wavefunctions $(\cos K_i\gamma, \sin K_i\gamma)$ are of symmetry (A_{ud}, A_{gd}) for K_i odd and (A_{gs}, A_{us}) for K_i even (A_{gs} for $K_i=0$).

Table 15-15

The $C_{2v}(M)$ subgroup of $G_4(EM)$, and the reverse-correlation species in $G_4(EM)$

C_{2v}:	E	a	E^*ab	E^*b	:	$G_4(EM)$ species
A_1:	1	1	1	1	:	$A_{gs} \oplus A_{ud}$
A_2:	1	1	−1	−1	:	$A_{us} \oplus A_{gd}$
B_1:	1	−1	1	−1	:	$B_{gs} \oplus B_{ud}$
B_2:	1	−1	−1	1	:	$B_{us} \oplus B_{gd}$

The result of correlating the torsional levels labeled v_4, v_4^t and K_i using the $G_4(EM)$ symmetry labels is given in Fig 15-13. In this diagram we have introduced $\Gamma = 1, 2, 3$ and 4 to label the four components into which each v_4 level is split [Flaud, Camy-Peyret, Johns and Carli (1989) use τ instead of Γ]. These four levels that are split apart by torsional tunneling have respective symmetries A_{gs}, A_{gd}, A_{ud} and A_{us}, but this order of the symmetry labels for the split levels is only true if the *trans* barrier is smaller than the *cis* barrier. The $\Gamma = 2$ (A_{gd}) and $\Gamma = 3$ (A_{ud}) components will switch in energy order if the *trans* barrier is larger than the *cis* barrier. The reader can show this by drawing the alternative correlation diagram in which the central torsional levels (labeled v_4^c in this case) are those of the C_{2v} molecule having an insuperable *trans* barrier. If the *cis* barrier is so high that there is no observable tunneling through it then components 1 and 2 would be degenerate and components 3 and 4 would also be degenerate. This is the situation observed by Flaud, Camy-Peyret, Johns and Carli (1989) in the $v_4 = 0$ torsional ground state of the vibrational ground state, and the observed energy of the $\Gamma = (3,4)$ component ($v_4^t = 1$) above the $\Gamma = (1,2)$ component ($v_4^t = 0$) is 11.4372 cm^{-1} as a result of tunneling through the *trans* barrier.

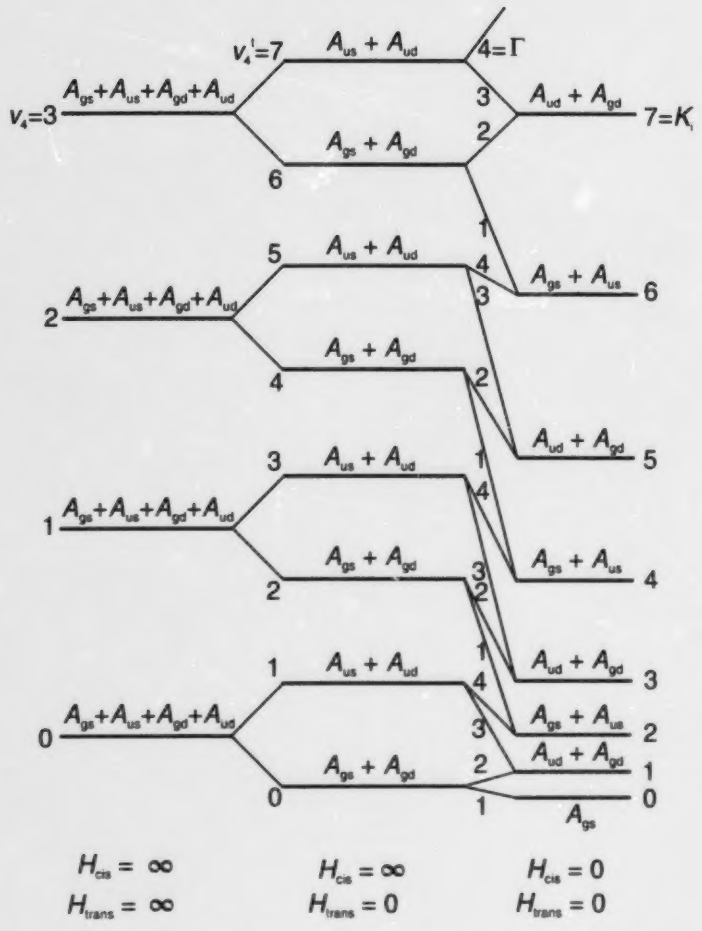
$v_4=3$
$A_{gs}+A_{us}+A_{gd}+A_{ud}$
$v_4^t=7$
$A_{us}+A_{ud}$
$A_{gs}+A_{gd}$
6
$4=\Gamma$
3
2
$A_{ud}+A_{gd}$
$7=K_t$
5
$A_{us}+A_{ud}$
2
$A_{gs}+A_{us}+A_{gd}+A_{ud}$
4
$A_{gs}+A_{gd}$
1
4
3
$A_{gs}+A_{us}$
6
2
$A_{ud}+A_{gd}$
5
3
$A_{us}+A_{ud}$
1
$A_{gs}+A_{us}+A_{gd}+A_{ud}$
2
$A_{gs}+A_{gd}$
1
4
3
2
$A_{gs}+A_{us}$
4
1
$A_{us}+A_{ud}$
0
$A_{gs}+A_{us}+A_{gd}+A_{ud}$
0
$A_{gs}+A_{gd}$
1
4
3
2
1
$A_{ud}+A_{gd}$
3
$A_{gs}+A_{us}$
2
$A_{ud}+A_{gd}$
1
A_{gs}
0
$H_{cis}=\infty$
$H_{trans}=\infty$
$H_{cis}=\infty$
$H_{trans}=0$
$H_{cis}=0$
$H_{trans}=0$

Fig. 15-13. A correlation diagram for the torsional energy levels of the hydrogen peroxide molecule. Levels with a given v_4 torsional quantum number label are not split when both the *trans* barrier H_{trans} and the *cis* barrier H_{cis} are insuperable. Levels with a given v_4^t torsional quantum number label are not split when the *cis* barrier is insuperable. The K_t torsional quantum number is appropriate in the low torsional barrier limit. The levels labeled Γ = 1, 2, 3 and 4 have symmetries A_{gs}, A_{gd}, A_{ud}, and A_{us} respectively.

To calculate the rotation-torsion energy levels we use a rotation-torsion Hamiltonian of the form given in Eq. (15-5) above where ρ is replaced by

γ. This Hamiltonian can be subjected to a contact transformation that puts it into a form in which only the xx, yy, zz, xz, and $\gamma\gamma$ elements of $\boldsymbol{\mu}^{\text{ref}}$ are nonvanishing, and the torsional Hamiltonian is as given in Eq. (15-22) above. Note that in solving this equation one must allow γ to range from 0 to 2π which means the torsional angle τ ranges from 0 to 4π. A general expansion for the potential is as given in Eq. (15-50) above (with ρ replaced by γ) and the only terms that are of symmetry A_{gs}, and which can therefore be nonvanishing, are the $\cos n\gamma$ terms having n even. Flaud, Camy-Peyret, Johns and Carli (1989) [see Eq. (8) in their paper] use terms in the potential up to $n = 8$ in a fitting to their experimental results.

Introducing tunneling through the *cis* barrier, which will resolve the degeneracies of the $\Gamma = (1,2)$ components [and separately of the $\Gamma = (3,4)$ components], brings in an interesting symmetry consideration. The total rotation-torsion-vibrational-electronic wavefunctions have to be of s symmetry since they must be invariant to E' which does not affect the space fixed coordinates. From the transformation properties of the Euler angles we can determine that the rotational wavefunctions are of s symmetry if K is even and of d symmetry if K is odd. Thus in the ground vibronic state, which is of s symmetry, a torsional component of s symmetry can only have even K, and a torsional component of d symmetry can only have odd K. (In the vibrational ground state of dimethylacetylene torsional states of even K_i can only have even K, and torsional states of odd K_i can only have odd K for the same reason.) The $\Gamma = 1$ and 4 components are of s symmetry and the $\Gamma = 2$ and 3 components are of d symmetry. This means that in the vibronic ground state the torsional components having $\Gamma = 1$ and 4 can only have K even, whereas the components having $\Gamma = 2$ and 3 can only have K odd. Thus there is no value of K for which both members of a pair of components, whose energies are split apart by tunneling through the *cis* barrier, will occur. The *cis* tunneling will not produce any splittings of the rotational levels, but rather a staggering of the energies of the K even states with respect to the K odd states. As a result a fitting, using a single Watsonian, of the rotational levels in a given torsional state labeled v_4^t will only fit to experimental precision if the effect of the *cis* tunneling is negligible. Flaud, Camy-Peyret, Johns and Carli (1989) find that for the $v_4 = 2$ and 3 states the staggering is significant, and to take it into account they use a Watsonian matrix where the $\Gamma = 1$ and 2 components (the same being true for the $\Gamma = 3$ and 4 components) are considered simultaneously but are allowed to have different values for the band centers and distortion constants, i.e., the K even and K odd sets of levels are fitted using different values for the band centers and distortion constants. The difference between the band centers can be considered as the value of the *cis* tunneling splitting. By making such a fitting Flaud, Camy-Peyret, Johns and Carli (1989) were able to determine that the *cis* barrier height is 2560 cm^{-1}, the *trans* barrier height is 387 cm^{-1}, and the equilibrium torsional (dihedral) angle is 112°. From this special Watsonian fitting the *cis* splitting of the $v_4^t = 6$ level, between the $\Gamma = 1$ and 2 components of the $v_4 = 3$ state, has been determined by Camy-Peyret, Flaud, Johns and Noël (1992) to be 0.0487 cm^{-1}; the $v_4^t = 6$ level is determined to be

1000.9 cm^{-1} above the $v_4^t = 0$ level.

15.4.6 Ethylene

There are interesting similarities and differences in the symmetry and spectroscopy of the ethylene molecule as compared to that for the hydrogen peroxide and dimethylacetylene molecules considered above. Our discussion here is from the results presented in the papers of Merer and Watson (1973), and Watson, Siebrand, Pawlikowski and Zgierski (1996), to which the reader should refer for more details. In its ground electronic state (the N state) ethylene is a planar molecule of $\boldsymbol{D}_{2h}$ symmetry with a torsional barrier of about 20000 cm^{-1} [Wallace (1989)], and the effects of torsional tunneling within this state have not been observed. Thus whereas dimethylacetylene has a very low torsional barrier, and hydrogen peroxide has two intermediate torsional barriers, ethylene has an insuperably high barrier. One might wonder why we discuss it in this chapter. The reason is that we wish to interpret experimental results involving transitions between the levels of the N state and the levels of the V electronic excited state which has $\boldsymbol{D}_{2d}$ symmetry. In order to understand properly such results it is necessary to allow complete internal rotation in the wavefunctions of the two states. As discussed in Chapter 3, in Section 3.5, elements of the CNPI group such as (12) and (34) now become feasible (i.e., useful), and the MS group we need for a satisfactory symmetry classification of the states becomes the group $\boldsymbol{G}_{16}$ (see Table A-25).

And, just as for dimethylacetylene and hydrogen peroxide, we need the EMS group in order to be able to classify the separate rotational, torsional and vibronic wavefunctions of the ethylene molecule. The character table of $\boldsymbol{G}_{16}$(EM) is given in Table A-32. The defined effect of each of the generating elements a, b, c and E' on the Euler angles is given in Table 15-16, where these operations have the same effect on the space fixed coordinates as the MS group elements $(1423)(56)^*$, $(13)(24)(56)$, E^* and E respectively. We follow the same notation for the irreducible representations as used by Merer and Watson (1973). With this definition for the Euler angle transformations the operation bc, which has the same effect on the space fixed coordinates as $(13)(24)(56)^*$, does not change the Euler angles, and [just as with the operation ab in $\boldsymbol{G}_4$(EM)] it is appropriate to use it to define the g and u label on the irreducible representations. As a result the rotational wavefunctions all have to be of g symmetry as usual. In a similar way the effect of the operation a gives the A/B symmetry, the effect of b gives the 1/2 subscript and the effect of c gives the $+/-$ superscript. This labeling is redundant for the A and B species but it is useful. Since b does not change γ all torsional wavefunctions have to be of the 'subscript 1' type. For the dimethylacetylene and hydrogen peroxide molecules the EMS group is the direct product of the MS group and the group $\{E, E'\}$, but $\boldsymbol{G}_{16}$(EM) does not have a direct product structure. The double valued irreducible representations (those having character under E' of opposite sign to that under E) are the four doubly degenerate representations at the bottom of the character table;

the other irreducible representations are single valued and the only symmetries possible for the rovibronic states. As with dimethylacetylene and hydrogen peroxide, the fact that E' has equivalent rotation R_z^{π} means that rotational states having odd K_a are changed in sign by E', and hence transform as a double valued representation, whereas rotational states having even K_a transform as a single valued representation.

Table 15-16

The transformation properties of θ, ϕ, χ and γ for ethylene under the effect of the generating operations of $G_{16}(\mathrm{EM})^a$

E	a	b	c	E'
θ	θ	$\pi-\theta$	$\pi-\theta$	θ
ϕ	ϕ	$\phi+\pi$	$\phi+\pi$	ϕ
χ	$\chi+(\pi/2)$	$-\chi$	$-\chi$	$\chi+\pi$
γ	$(\pi/2)-\gamma$	γ	$\pi-\chi$	$\gamma+\pi$

$^a\phi, \chi, \gamma$ are mod 2π, $0 \leq \theta \leq \pi$.

We want to understand the selection rules on the torsional quantum number v_4 in the V-N resonant Raman spectrum of ethylene, i.e., the Raman spectrum of ethylene when the Raman exciting radiation is resonant with the V-N electronic transition.[12] From Eqs. (14-120) and (14-122) we see that allowed Raman transitions within the N state are between states that have the same rovibronic symmetry. Using the group $\boldsymbol{D}_{2h}$ the torsional normal coordinate Q_4 is of species A_u, and (of course) the rotational states are all of g species (see Table 12-10). So we expect allowed rotation-torsion transitions to satisfy Δv_4 = even. The problem is to account for the appearance of bands [see Sension and Hudson (1989) and references therein] that satisfy the selection rule Δv_4=odd, and which are, therefore of the type u ↔ g in $\boldsymbol{D}_{2h}$.

The selection rule Δv_4 = even is obtained if we just consider $\boldsymbol{D}_{2h}$ symmetry. This symmetry is appropriate if it is satisfactory to allow only infinitesimal displacements away from the planar $\boldsymbol{D}_{2h}$ geometry in the calculation of the two successive electric dipole matrix elements needed to calculate the intensity in the resonant Raman effect. Since the V state has $\boldsymbol{D}_{2d}$ equilibrium structure we expect to see a long Franck-Condon progression [see Chapter 14] in the torsional vibration, and we must allow for complete internal rotation in the calculation of the electric dipole matrix elements. As a result it becomes necessary to use the $\boldsymbol{G}_{16}(\mathrm{EM})$ group for the simultaneous symmetry classification of N and V

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[12] The reader may wish to reread Section 14.3 at this point; in the notation of that section the resonant Raman effect occurs when $\tilde{\nu}_{ji} = \tilde{\nu}$. As a result there is resonantly enhanced intensity [see, for example, Siebrand and Zgierski (1979)].

electronic state energy levels. Doing this resolves the problem of accounting for the appearance of the Δv_4=odd bands in the spectrum, as we now show.

From the rotational species given in Table 12-10, the fact that Q_4 is A_u and the fact that the N electronic state is of symmetry A_g, we deduce the $\boldsymbol{D}_{2h}$ symmetry species of the rotation-torsion energy levels in the N state to be as given in Table 15-17. Using the reverse correlation table for $\boldsymbol{D}_{2h}$ to $\boldsymbol{G}_{16}$(EM) the species in $\boldsymbol{G}_{16}$(EM) are obtained; the double valued species, which do not occur, are placed in parentheses. We see that Δv_4 = odd transitions are allowed in the Raman effect but with K_a = odd only. Thus, for example, in the $v_4 = 1 \leftarrow 0$ band, only the K_aK_c = oo ← oe (both E^+) and oe ← oo (both E^-) subbands will appear, whereas in the $v_4 = 2 \leftarrow 0$ band the ee ← ee (both $A_{1g}{}^+ \oplus B_{1g}{}^+$), eo ← eo (both $A_{2g}{}^- \oplus B_{2g}{}^-$), oe ← oe (both E^+), and oo ← oo (both E^-) subbands will appear. The calculation of the relative intensity of the Δv_4 odd and even bands has been considered by Watson, Siebrand, Pawlikowski and Zgierski (1996). The rotational structure has yet to be resolved in these bands.

Table 15-17

The species of the rotation-torsion levels of the N electronic state of ethylene[a].

v_4	K_aK_c	$\boldsymbol{D}_{2h}(\mathrm{M}) \rightarrow \boldsymbol{G}_{16}(\mathrm{EM})$
even	ee	$A_g \rightarrow A_{1g}{}^+ \oplus B_{1g}{}^+ \oplus (E_1)$
	eo	$B_{1g} \rightarrow A_{2g}{}^- \oplus B_{2g}{}^- \oplus (E_2)$
	oe	$B_{3g} \rightarrow E^+ \oplus (E_g)$
	oo	$B_{2g} \rightarrow E^- \oplus (E_g)$
odd	ee	$A_u \rightarrow A_{1u}{}^- \oplus B_{1u}{}^- \oplus (E_1)$
	eo	$B_{1u} \rightarrow A_{2u}{}^+ \oplus B_{2u}{}^+ \oplus (E_2)$
	oe	$B_{3u} \rightarrow E^- \oplus (E_u)$
	oo	$B_{2u} \rightarrow E^+ \oplus (E_u)$

[a] The double valued species in $\boldsymbol{G}_{16}$(EM), which do not occur, are placed in parentheses.

Using the reverse correlation table in the purely torsional problem the levels of even v_4 value have $\boldsymbol{G}_{16}$(EM) species $A_{1g}{}^+ \oplus B_{1g}{}^+ \oplus E_1$ and the levels of odd v_4 value have species $A_{1u}{}^- \oplus B_{1u}{}^- \oplus E_1$. Torsional tunneling would split each level into three levels, two of which have (single valued) A/B species and K_a even and the third of which has (double valued) E_1 species and K_a odd. There would be the same kind of staggering between even and odd K_a as a result of torsional tunneling as there is in hydrogen peroxide; the levels with even K_a could be split into two as a result of torsional tunneling, whereas the levels with odd K_a cannot show any torsional tunneling splitting.

15.4.7 Methylene

The present subsection considers the problem of calculating the rovibronic energies of $\tilde{X}\,^3B_1$ CH_2 as an example to show how quasilinear molecules are treated. There are some other discussions of the spectroscopy of methylene in Chapters 13 and 14. In Chapter 13 the $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ electronic states are used as an example of the Renner effect [see Figs. 13-7 and 13-8 on pages 374 and 376, respectively], and the singlet-triplet interaction between the $\tilde{X}\,^3B_1$ ground electronic state and the $\tilde{a}\,^1A_1$ first excited electronic state is mentioned in connection with Fig. 13-14 on page 398. In Chapter 14 we briefly consider the spin splittings in the $\tilde{X}\,^3B_1$ electronic state, and we use the $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ states as an example of intensity stealing caused by the Renner effect.

For quasilinear molecules difficulties arise because an element of $\boldsymbol{\mu}^{\text{ref}}$ is a singular function of ρ [see Eq. (15-5) and the discussion after it]. The HBJ treatment was specifically set up for such molecules, and developments of the HBJ Hamiltonian have lead to the rigid bender, semirigid bender, and nonrigid bender Hamiltonians discussed above in connection with Eq. (15-16). The reader is referred to the references cited above for the details, and particularly to the review by Jensen (1983a). The spectroscopic investigation of CH_2, in which theoretical interpretations and predictions made using these Hamiltonians were very successful, is reviewed by Bunker (1985). A more recent development of the HBJ Hamiltonian is the Morse oscillator rigid bender internal dynamics (MORBID) Hamiltonian that we discuss below. The alternative approach using the exact kinetic energy operator and variational theory is described in Section 13.2.5 and will not be discussed further in this section.

As can be recognized from Fig. 13-14 the equilibrium structure of $\tilde{X}\,^3B_1$ state methylene is bent but the barrier to linearity in the potential energy function is lower than 2000 cm^{-1}. This means that there will be large amplitude bending and the linear geometry is accessible, i.e., $\tilde{X}\,^3B_1$ CH_2 is quasilinear. The method for calculating rotation and vibration energies for nonlinear rigid molecules is given in Chapters 10 and 11, and it is appropriate if the potential energy surface of the molecule under study has an insuperable barrier to linearity so that the linear configuration is inaccessible. Alternatively the method for rigid linear molecules is given in Chapter 17, and it can be successfully applied if the equilibrium structure of the molecule is linear and if its potential energy surface is such that it can only carry out small oscillations around the linear configuration. We cannot use either of these rigid molecule approaches for $\tilde{X}\,^3B_1$ methylene. Instead we treat a quasilinear molecule as a nonrigid molecule and develop a special rotation-contortion Hamiltonian in which the bending coordinate is the contortion.

To develop the treatment we take the contortion coordinate ρ as the supplement of the bond angle in the reference configuration as shown in Fig. 15-14. The figure shows the relationship between the instantaneous configuration [with variable bond lengths r_{12} and r_{32}, where r_{j2} is the instantaneous value of the distance from the "terminal" nucleus j (labeled 1 or 3) to the "central" nucleus labeled 2, and bond angle supplement $\bar{\rho}$] and the reference configuration [with constant bond lengths r_{12}^{e} and r_{32}^{e}, taken as the equilibrium values of r_{12} and r_{32}, and bond angle supplement ρ]. The z axis is the molecule fixed axis with the smallest moment of inertia; it coincides with the molecular axis at linear geometries. See also Fig. 2 of HBJ.

For a symmetrical ABA triatomic molecule the MS group is $\boldsymbol{C}_{2\mathrm{v}}(\mathrm{M}) = \{E,(13),E^*,(13)^*\}$ where the identical nuclei A are labeled 1 and 3, and for an unsymmetrical triatomic molecule the MS group is $\boldsymbol{C}_{\mathrm{s}}(\mathrm{M}) = \{E,E^*\}$. The bending (contortional) coordinate ρ and its conjugate momentum $\hat{J}_\rho$ are both totally symmetric in the MS group. Therefore, the ρ-dependent matrix elements $\mu_{\alpha\beta}^{\mathrm{ref}}$ in Eq. (15-5) are all totally symmetric. With the molecule fixed axis system defined as in Fig. 15-14 the molecule fixed angular momentum components $(\hat{J}_x, \hat{J}_y, \hat{J}_z)$ of a $\boldsymbol{C}_{2\mathrm{v}}(\mathrm{M})$ molecule have the MS group symmetries B_2, A_2, and B_1, respectively [see Table A-5]. Since all the elements $\mu_{\alpha\beta}^{\mathrm{ref}}$ are totally symmetric in the MS group it follows that for the term $(1/2)\mu_{\alpha\beta}^{\mathrm{ref}}\hat{J}_\alpha\hat{J}_\beta$ in Eq. (15-5) to be totally symmetric in $\boldsymbol{C}_{2\mathrm{v}}(\mathrm{M})$ we must have $\alpha = \beta$. Thus, only the diagonal matrix elements μ_{xx}^{ref}, μ_{yy}^{ref}, μ_{zz}^{ref}, and $\mu_{\rho\rho}^{\mathrm{ref}}$ are nonvanishing for a triatomic molecule with $\boldsymbol{C}_{2\mathrm{v}}(\mathrm{M})$ symmetry.

For a $\boldsymbol{C}_{\mathrm{s}}(\mathrm{M})$ molecule ρ, $\hat{J}_\rho$ and $\hat{J}_x$ are totally symmetric (i.e., of A' symmetry) in the MS group, and $\hat{J}_y$ and $\hat{J}_z$ have A'' symmetry [see Table A-2]. Consequently, in this case the elements μ_{xx}^{ref}, μ_{yy}^{ref}, μ_{zz}^{ref}, $\mu_{\rho\rho}^{\mathrm{ref}}$, $\mu_{yz}^{\mathrm{ref}} = \mu_{zy}^{\mathrm{ref}}$ and $\mu_{x\rho}^{\mathrm{ref}} = \mu_{\rho x}^{\mathrm{ref}}$ can be nonvanishing. However, we are free to choose the orientation of the molecule fixed axis system relative to the reference configuration. In applications of HBJ theory to triatomic molecules it is customary to use this freedom of choice to eliminate $\mu_{x\rho}^{\mathrm{ref}}$. The molecule fixed axes are chosen so that the molecule is in the yz plane, but the angle ϵ [Fig. 15-14] is determined as a function of ρ so that $\mu_{x\rho}^{\mathrm{ref}} = \mu_{\rho x}^{\mathrm{ref}} = 0$. The function $\epsilon(\rho)$ for an unsymmetrical triatomic molecule was derived in HBJ and is given in Eq. (2.7) of Jensen (1983a). For a triatomic molecule with $\boldsymbol{C}_{2\mathrm{v}}(\mathrm{M})$ symmetry the reference configuration has $C_{2\mathrm{v}}$ point group symmetry, the y axis coincides with the C_2 axis, and $\epsilon = \rho/2$.

In the treatment of the Renner effect given in Chapter 13 we point out that the $\boldsymbol{\mu}$-matrix element μ_{zz} is singular at $\rho = 0$ [i.e., when the molecule is linear; see Eq. (13-176)]. Similarly the $\boldsymbol{\mu}^{\mathrm{ref}}$-matrix element μ_{zz}^{ref} is also singular at $\rho = 0$. The value of μ_{zz}^{ref} near $\rho = 0$ can be related to the value of the function $\mu_{\rho\rho}^{\mathrm{ref}}$ which is a slowly varying positive-valued function of ρ. If we let $\mu_{\rho\rho}^{\mathrm{ref}}(0)$ (> 0) denote the value of this function at $\rho = 0$ then

$$\mu_{zz}^{\mathrm{ref}} \approx \frac{\mu_{\rho\rho}^{\mathrm{ref}}(0)}{\rho^2}. \tag{15-94}$$

This behavior causes the determinant μ of $\boldsymbol{\mu}^{\mathrm{ref}}$ to be singular at $\rho = 0$. The nuclear-mass-dependent correction to the contortional potential [the third term

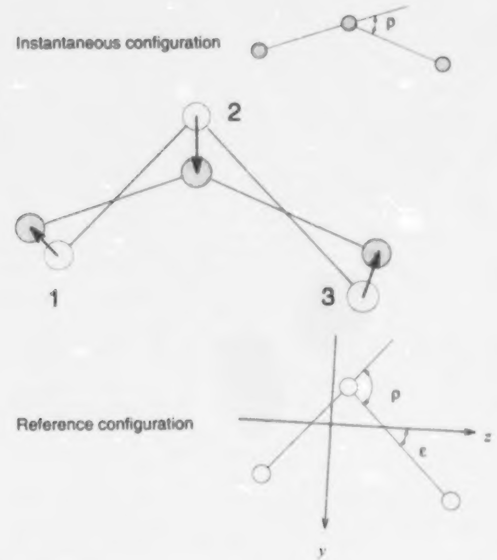

Fig. 15-14. The definitions of the angles $\bar{\rho}$, ρ, and ϵ and the molecule fixed axis system used in the HBJ Hamiltonian for a triatomic molecule. The open circles are the positions of the nuclei in the reference configuration; the shaded circles are their instantaneous positions. The angle $\bar{\rho}$ is the instantaneous value of the supplement of the bond angle and ρ is the corresponding angle in the reference configuration. The angle ϵ depends on ρ and is determined so that $\mu^{\mathrm{ref}}_{x\rho} = 0$. The (x, y, z) axes form a right-handed axis system where the x axis is perpendicular to the molecular plane.

in Eq. (15-5)] can be rewritten as

$$\frac{1}{2}\mu^{1/4}[J_\rho\mu^{-1/2}\mu^{\mathrm{ref}}_{\rho\rho}(J_\rho\mu^{1/4})] = \frac{\hbar^2}{2}\,\mu^{\mathrm{ref}}_{\rho\rho}\,g(\rho) + \frac{1}{2}\mu^{-1/4}\left(j_\rho\mu^{\mathrm{ref}}_{\rho\rho}\right)\left(j_\rho\mu^{1/4}\right), \tag{15-95}$$

where the dimensionless function

$$g(\rho) = -\mu^{1/4}\frac{d}{d\rho}\left[\mu^{-1/2}\frac{d}{d\rho}\left(\mu^{1/4}\right)\right]. \tag{15-96}$$

For ρ near 0 we can approximate $g(\rho)$ as

$$g(\rho) \approx -\frac{1}{4\rho^2}, \tag{15-97}$$

i.e., the first term on the right hand side of Eq. (15-95) is singular at $\rho = 0$. The second term can be shown to be non-singular and small; it can be neglected in the zero order treatment of a triatomic molecule.

For a triatomic molecule the terms

$$\frac{1}{2}\mu^{\mathrm{ref}}_{zz}\hat{J}^2_z \text{ and } \frac{\hbar^2}{2}\,\mu^{\mathrm{ref}}_{\rho\rho}\,g(\rho)$$

in the Hamiltonian $\hat{H}_{\mathrm{rc}}$ of Eq. (15-5) both have a strong modifying effect on the bending motion because of their singularity at $\rho = 0$. In the zero order treatment it is not a satisfactory approximation to separate these terms from the other important bending terms $(1/2)\mu^{\mathrm{ref}}_{\rho\rho}\hat{J}^2_\rho$, $(1/2)(\hat{J}_\rho\,\mu^{\mathrm{ref}}_{\rho\rho})\hat{J}_\rho$ and $V_0(\rho)$ in Eq. (15-22). Thus we cannot separate the bending and z-axis rotation in zero order, which means that for a quasilinear triatomic molecule we treat them together and replace Eq. (15-22) by

$$\hat{H}_{\mathrm{con},z} = \frac{1}{2}\mu^{\mathrm{ref}}_{\rho\rho}\hat{J}^2_\rho + \frac{1}{2}(\hat{J}_\rho\mu^{\mathrm{ref}}_{\rho\rho})\hat{J}_\rho + \frac{\hbar^2}{2}\,\mu^{\mathrm{ref}}_{\rho\rho}\,g(\rho) + \frac{1}{2}\mu^{\mathrm{ref}}_{zz}\hat{J}^2_z + V_0(\rho). \qquad (15\text{-}98)$$

From the fact that $\hat{J}_z = -i\hbar\partial/\partial\chi$ commutes with $\hat{H}_{\mathrm{con},z}$ it follows that we can express the eigenfunctions of $\hat{H}_{\mathrm{con},z}$ as

$$\Phi_{\mathrm{con},z}(\rho,\chi) = \psi^{(k)}_{\mathrm{con},z}(\rho)\,\left(\mu^{\mathrm{ref}}_{\rho\rho}\right)^{-1/2}\,\frac{1}{\sqrt{2\pi}}\exp(ik\chi), \qquad (15\text{-}99)$$

where k is an integer and the function $\psi^{(k)}_{\mathrm{con},z}(\rho)$ satisfies the equation [see Eq. (13) of Bunker and Stone (1972)]

$$\frac{d^2\psi^{(k)}_{\mathrm{con},z}(\rho)}{d\rho^2} = \left\{f_1(\rho) + \frac{\mu^{\mathrm{ref}}_{zz}}{\mu^{\mathrm{ref}}_{\rho\rho}}k^2 + \frac{2}{\hbar^2\mu^{\mathrm{ref}}_{\rho\rho}}\left(V_0(\rho) - E^{(k)}_{\mathrm{con},z}\right)\right\}\psi^{(k)}_{\mathrm{con},z}(\rho), \qquad (15\text{-}100)$$

where $E^{(k)}_{\mathrm{con},z}$ is the eigenvalue of $\hat{H}_{\mathrm{con},z}$ corresponding to the eigenfunction in Eq. (15-99), and we have introduced the dimensionless function

$$f_1(\rho) = \mu^{1/4}\left(\mu^{\mathrm{ref}}_{\rho\rho}\right)^{-1/2}\frac{d^2}{d\rho^2}\left[\mu^{-1/4}\left(\mu^{\mathrm{ref}}_{\rho\rho}\right)^{1/2}\right]. \qquad (15\text{-}101)$$

The difference $g(\rho) - f_1(\rho)$ is non-singular and small for all ρ, so for ρ near 0 we have from Eq. (15-97)

$$f_1(\rho) \approx -\frac{1}{4\rho^2}. \qquad (15\text{-}102)$$

Equation (15-100) is solved numerically [see Eqs. (14)-(19) of Bunker and Landsberg (1977), and Section 6 of Jensen (1983a)], and we obtain numerical values of the functions $\psi^{(k)}_{\mathrm{con},z}(\rho)$ over a grid of ρ values from $\rho = 0$ to ρ_{max}. We choose the grid fine enough and ρ_{max} large enough to ensure convergence. For $\tilde{X}\,{}^3B_1$ state methylene a ρ_{max} value of 1.9 rad with 400 grid points is sufficient.

It is of interest to understand the form of the wavefunctions near $\rho = 0$. For $\rho = 0$ the two first terms in the { } braces of Eq. (15-100) are singular. Thus, for ρ near 0, they dominate over the third, non-singular term. This term can be neglected and the two singular terms can be approximated by Eqs. (15-94) and (15-102), respectively, so that we have

$$\frac{d^2\psi^{(k)}_{\mathrm{con},z}}{d\rho^2} \approx \frac{k^2 - 1/4}{\rho^2}\,\psi^{(k)}_{\mathrm{con},z}(\rho) \tag{15-103}$$

with the solution

$$\psi^{(k)}_{\mathrm{con},z}(\rho) \approx C'\rho^{|k|+1/2}, \tag{15-104}$$

where C' is a constant. As discussed above, $\mu^{\mathrm{ref}}_{\rho\rho}$ has the positive value $\mu^{\mathrm{ref}}_{\rho\rho}(0)$ at $\rho = 0$, so the eigenfunction of $\hat{H}_{\mathrm{con},z}$, $\Phi_{\mathrm{con},z}(\rho,\chi)$ from Eq. (15-99), is given by

$$\Phi_{\mathrm{con},z}(\rho,\chi) \approx C\rho^{|k|+1/2}\frac{1}{\sqrt{2\pi}}\exp(ik\chi), \tag{15-105}$$

for ρ near 0, where $C = C'\left(\mu^{\mathrm{ref}}_{\rho\rho}(0)\right)^{-1/2}$.

Having obtained the eigenfunctions $\Phi_{\mathrm{con},z}(\rho,\chi)$ [Eq. (15-99)] of $\hat{H}_{\mathrm{con},z}$, the matrix representation of $\hat{H}_{rc}$ [Eq. (15-5)] is diagonalized in a basis of functions

$$\Phi^{(\mathrm{b})}_{rc} = \left\{S_{Jkm}(\theta,\phi)[1/(2\pi)]^{1/2}\exp(ik\chi)\right\}\psi^{(k)}_{\mathrm{con},z}(\rho)\left(\mu^{\mathrm{ref}}_{\rho\rho}\right)^{-1/2}, \tag{15-106}$$

where the superscript '(b)' means 'basis' [see Eq. (16) of Bunker and Stone (1972)]. In Eq. (15-106), the (θ,ϕ,χ)-dependent function in the { } braces [obtained by combining the $S_{Jkm}(\theta,\phi)$ factor with the factor $\exp(ik\chi)/\sqrt{2\pi}$ from Eq. (15-99)] is a symmetric top function [see Eq. (11-16)].

The Hamiltonian $\hat{H}_{\mathrm{con},z}$ of Eq. (15-98) describes the bending motion and the rotation about the z axis for a triatomic molecule. In the general treatment given here, we cannot separate these two motions since, for example, the degree of rotational excitation, defined by k, determines the behavior of the bending wavefunctions near linearity as given in Eq. (15-105). Only in the event that the bending potential energy $V_0(\rho)$ has its minimum at $\rho = \rho_e > 0$ and is such that on the time scale of the experiment being interpreted, the molecule can only carry out small oscillations around $\rho = \rho_e$ without approaching the linear configuration, would it be permissible to approximate μ^{ref}_{zz} by the constant value $\mu^{\mathrm{ref}}_{zz}(\rho_e)$. If we make this approximation we can separate the rotation around the z axis from the bending, but this description will break down for bending states so highly excited that the linear configuration becomes accessible.

The HBJ Hamiltonian for a quasilinear molecule has been applied to linear chain molecules such as HCNO [see Bunker, Landsberg, and Winnewisser (1979), and Jensen (1983b)] and C_3O_2 [see Bunker (1980), and Jensen (1984)].

For a triatomic molecule the treatment of rotation and bending motion outlined above is combined with a harmonic-oscillator treatment of the stretching motion to give zero order rotation-bending-stretching energies. In the nonrigid-bender approach the anharmonic terms in the potential energy function for the stretching motion and all stretch-bend interaction terms in the rotation-vibration Hamiltonian are treated by means of perturbation theory. The nonrigid bender Hamiltonian obtained in this way is an effective rotation-bending Hamiltonian designed for the calculation (or fitting) of the rotation bending energy levels of any stretching state of a triatomic molecule. It was very successful in the fitting and predicting of rotation bending levels in methylene [see Bunker (1985)]. However, it is not designed for the accurate prediction of the stretching energies since it uses perturbation theory, and Jensen (1992) shows that it is unreliable for such calculations. Accurate predictions are desirable for the purpose of aiding the experimental search for the ν_1 and ν_3 CH stretching fundamental bands. In order to make accurate calculations of rotation-bending and stretching states of a triatomic molecule the MORBID (Morse Oscillator Rigid Bender Internal Dynamics) Hamiltonian and computer program [Jensen (1988a, 1988b, 1992, 1994)] were developed.

The MORBID approach is based on the HBJ Hamiltonian for a triatomic molecule. It describes the rotation by the Euler angles (θ, ϕ, χ) and the bending vibration of the triatomic molecule by the coordinate ρ, defined as the supplement of the bond angle in the reference configuration. The coordinates $(\theta, \phi, \chi, \rho)$ are defined by using Eckart and Sayvetz conditions as explained above. However, the HBJ Hamiltonian is transformed to a form where the stretching motion is described by the geometrically defined coordinates r_{12} and r_{32}. The rotation-vibration energies and wavefunctions are obtained in a variational calculation [*i.e.*, by diagonalization of a matrix representation of the Hamiltonian]. The basis functions used for the diagonalization are obtained as products of the functions $\Phi_{\rm rc}^{(b)}$ [Eq. (15-106)] and Morse oscillator eigenfunctions [see, for example, Efremov (1977) or Špirko, Jensen, Bunker, and Čejchan (1985)] describing the stretching vibrations. In order to implement the Eckart and Sayvetz conditions it is necessary to approximate the kinetic energy operator by a fourth order expansion in the stretching vibrational coordinates. No approximations are made for the bending motion. Owing to the minimization of the coupling between the different types of motion resulting from the Eckart and Sayvetz conditions, MORBID calculations require significantly less computer capacity than calculations based on kinetic energy operators expressed in terms of geometrically defined coordinates and employing a body fixed axis system [see Section 13.2.5]. However, the MORBID results will differ slightly from those of such "non-Eckart-Sayvetz" calculations because of the approximations in the MORBID kinetic energy operator.

In Table 15-18 we compare three MORBID predictions of the fundamental energies of $^{12}CH_2$ made with three different potential energy functions, two *ab initio* potentials and one obtained by Jensen and Bunker (1988) in a least-squares fitting to experimental spectroscopic data using the MORBID program. It is seen that the predictions for the ν_1 and ν_3 energies are close in the three calculations, and they should be of assistance in the experimental search for

Table 15-18

Vibrational energies of $^{12}CH_2$ (in cm^{-1}) predicted with the MORBID program

Reference	Method	ν_1	ν_2[b]	ν_3
Jensen (1988a)[a]	*ab initio*	2994	973	3212
Comeau, Shavitt, Jensen, and Bunker (1989)	*ab initio*	3015	974	3236
Jensen and Bunker (1988)	Fitting	2992	963	3214

[a] Potential energy surface from McLean, Bunker, Escribano, and Jensen (1987).

[b] The experimental value for the ν_2 energy is 963 cm^{-1} [Sears, Bunker, and McKellar (1982)].

the ν_1 and ν_3 fundamental bands. However, Jensen (1988c) has calculated the intensities of the rotation-vibration transitions for $\tilde{X}\,^3B_1$ CH_2 using the rotation-vibration wavefunctions obtained by the MORBID program and an *ab initio* dipole moment surface by Bunker and Langhoff (1983). These *ab initio* calculations predict that the ν_1 and ν_3 CH stretching fundamentals are very weak. Their integrated absorption coefficients [Eq. (14-3)] are typically two orders of magnitude smaller than those of the ν_2 band transitions, and this explains why they have not yet been observed.

The MORBID program has been applied to a large number of triatomic molecules other than methylene, and the appropriate references up to 1994 are listed by Jensen (1994) (for more recent applications, see also Section 15.4.8). Kozin and Jensen (1997) have extended the MORBID formalism to electronic states with $S > 0$, and they have calculated the fine structure splittings in $\tilde{X}\,^3B_1$ CH_2.

As a postscript to this subsection we say a few words about symmetry, about the bending angle ρ, and about the Euler angle χ. The MS group for a triatomic molecule [$\boldsymbol{C}_{2v}(M)$ or $\boldsymbol{C}_s(M)$] is independent of the height of the barrier to linearity. This is because there is never any tunneling through linearity and never any energy level splitting arising from penetration of the barrier at linearity for a triatomic molecule. The bending angle ρ is defined in the range $0 \leq \rho \leq \pi$ only, and the angle specifying the extent of the rotation about the z axis is χ which can range from 0 to 2π. With these two angles in these two ranges the molecule covers the entire space of bending and z axis rotation. The molecule never 'bends through' the linear configuration. Starting from a bent configuration if we change the Euler angle χ by π this will rotate the molecule around the z axis to the position 'on the other side' of the linear configuration. We are always careful in drawing the bending potential of a triatomic molecule [see Fig. 13-6 for example] only to present it for ρ in the allowed range of 0 to

π, and not to draw it from $-\pi$ to $+\pi$ which gives the false impression that a double minimum potential is involved for a bent molecule.

15.4.8 Hydrogen telluride

In highly excited rotational states centrifugal forces are strong, and they can cause such a large distortion of a molecule away from its equilibrium configuration that the molecule has to be treated as being nonrigid. An example of this is afforded by the H_2Te molecule, and by the related molecules H_2S, H_2Se, and H_2Po. For high values of J and K_a the rotation-vibration energy levels of these molecules cluster together in groups of four, and this cannot be understood easily using the Watsonian for the rotational energy levels of an asymmetric top[13] [see Eq. (13-126)]. A detailed discussion of the way to deal with the problem is given by Jensen, Osmann, and Kozin (1997) [see also the references therein]. The treatment leads to the introduction of a further feasibility requirement on the elements of the CNPI group when such clusters are unresolved.

In Section 13.2.4 we mention the analogous clustering pattern that emerges in the energy levels of spherical tops at high rotational excitation; this was discovered and explained by Dorney and Watson (1972). In methane for a given value of J there are[14] $2J+1$ rotational states that are degenerate in the rigid-rotor approximation. The symmetry species of these $2J+1$ states in the MS group $\boldsymbol{T}_d(M)$ is given in Table 12-12; the species for $J = 18$ is spelled out as an example in Eq. (13-134). Centrifugal distortion splits the levels apart but at high J the top eight states cluster together and the bottom six cluster together. Between these two energy level clusters the levels have a somewhat complicated pattern with no systematic clustering. Table III of Dorney and Watson (1972) gives numerical values of the centrifugal distortion contribution to the energies and we see, for example, that for $J = 18$ the eight centrifugal fine structure states having symmetry $A_1 \oplus F_1 \oplus F_2 \oplus A_2$ cluster close together at the top of the stack and the six states having symmetry $A_2 \oplus F_2 \oplus E$ cluster close together at the bottom; the remaining states (spanning $A_1 \oplus 2E \oplus 3F_1 \oplus 3F_2$) give nine levels that occur between these clusters. Dorney and Watson (1972) give a simple classical interpretation for the clustering in which they begin by writing the quartic centrifugal energy expression h_{cent} as a classical energy expression in the angular momentum $J = |\boldsymbol{J}|$. Using this expression they show that the highest value for h_{cent} $(8J^4/3)$ occurs when the molecule is rotating about one of the C_3 axes; there are four such axes and the molecule can rotate in two directions about each axis to give eight states in all. The lowest value of h_{cent} ($-4J^4$) occurs when the molecule is rotating about one of its S_4 axes; there are three such axes and thus six states. The 'centrifugal' rigidity of the molecule to rotation about the C_3 and S_4 axes is different, and this is the reason why the upper and lower sets of levels have different energy for a given amount of angular momentum. However, within the sets the centrifugal distortions are the same.

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[13] In order to obtain a satisfactory Watsonian fitting of the frequencies for transitions involving cluster levels, very many parameters must be varied. However, the energies calculated with the fitted parameter values do not provide a good extrapolation to levels not yet observed. An improvement can be obtained by a re-parameterization of the Watsonian, in which some of the higher order terms are expressed in terms of $\hat{J}^2$ and $\hat{J}^2 - \hat{J}_z{}^2$ rather than in terms of $\hat{J}^2$ and $\hat{J}_z{}^2$ [see Eq. (8) of Kozin, Belov, Polyansky, and Tretyakov (1992)].

[14] Neglecting the m-degeneracy.

Similar arguments explain the fourfold clustering of the rotational levels of H_2Te at high J. We will couch the explanation in the language of the *rotational energy surface* (RES) [see, for example, Harter and Patterson (1984)]. By doing so we can extend the definition of 'feasibility' for elements of the CNPI group in language involving the rotational energy surface that is similar to that used in Chapter 3 involving the potential energy surface.

A rotational energy surface is a three-dimensional radial plot of the energy of a molecule as a function of the direction of the total angular momentum $\boldsymbol{J}$ in the molecule fixed axis system (x, y, z). In this treatment $\boldsymbol{J}$ is a classical vector (as opposed to a vector of operators) of fixed length J with components J_x, J_y and J_z. Thus a rotational energy surface $E_J(\theta, \phi)$ is obtained by making the following substitutions[15]

$$\begin{aligned} J_x &\to J \sin\theta \cos\phi \\ J_y &\to J \sin\theta \sin\phi \\ J_z &\to J \cos\theta, \end{aligned} \tag{15-107}$$

in the Watsonian for the vibrational state under study. Makarewicz (1990) has shown how the RES can be obtained directly from the rotation-vibration Hamiltonian. In obtaining the RES, the magnitude of $\boldsymbol{J}$ in units of $\hbar$, $J = |\boldsymbol{J}|/\hbar \geq 0$, is chosen as one of the integer values 0, 1, 2, 3, ... allowed by quantum mechanics. Because we do this, and because we treat the vibrational motions quantum mechanically, we say that this is now a *semi*-classical calculation rather than a classical calculation. In the treatment of rotational motion proposed by Harter and Patterson (1984) the rotational energy surface plays much the same role as the potential energy surface in a study of vibrational motion. Since energy is conserved during the rotational motion, the possible trajectories of the tip of the angular momentum vector on the rotational energy surface (as the molecule rotates) correspond to intersections of the RES with constant energy surfaces; these constant energy surfaces are spheres. For H_2X molecules the theory of rotational energy surfaces is considered by Pavlichenkov and Zhilinskii (1988), Makarewicz and Pyka (1989), Makarewicz (1990), and by Kozin, Belov, Polyansky, and Tretyakov (1992).

In Fig. 15-15 we show part of the rotational energy level structure for a $H_2{}^{130}$Te molecule taken to be rigidly rotating in its equilibrium configuration with no centrifugal distortion [this equilibrium geometry is as determined by Gómez and Jensen (1997)]. The calculation of the rotational energies for a rigid

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[15] J, θ and ϕ are the spherical coordinates of $\boldsymbol{J}$ in the (x, y, z) axis system, and the angles have nothing to do with the Euler angles.

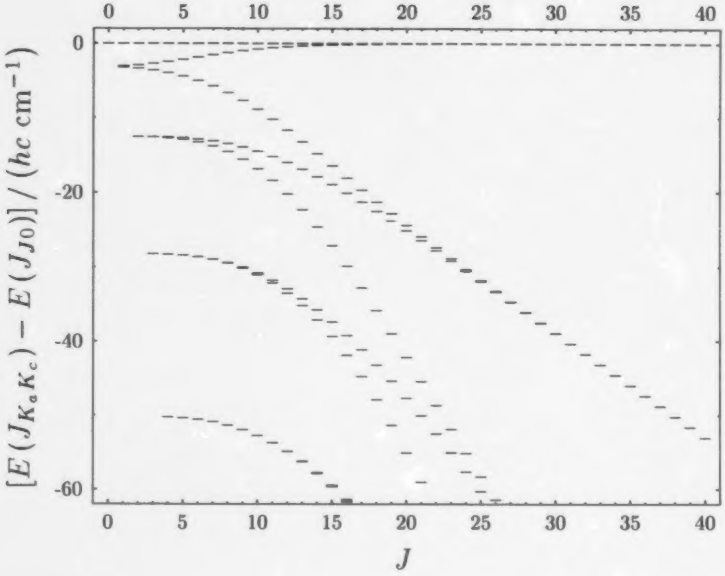

Fig. 15-15. The rotational energy level structure of a rigid $H_2{}^{130}Te$ molecule (taken to be in its equilibrium configuration). Term values are plotted relative to the highest term value for each J multiplet.

asymmetric top is discussed in Section 11.2.4. The pattern seen in Fig. 15-15 can be understood in terms of RES theory. For example, the figure shows that the two highest energies for each J value [with $(K_a, K_c) = (J, 0)$ and $(J, 1)$, respectively; see Section 11.2.4] become nearly degenerate for high J. On the RES of an asymmetric rigid rotor the maximum rotational energy for a given value of J is obtained when the angular momentum is directed along the a axis; choosing $z = a$, as in Fig. 15-16, this can be along either the positive $(+z)$ or the negative $(-z)$ direction. We say that the RES has two *symmetrically equivalent* stationary points in the $+z$ and $-z$ directions. The doubly degenerate energy cluster formed by the $(K_a, K_c) = (J, 0)$ and $(J, 1)$ energies for higher J values corresponds to the two smallest oval trajectories of $\boldsymbol{J}$ precessing around the $+z$ and $-z$ directions. In general, it can be seen that if the RES has a set of t symmetrically equivalent stationary points there will exist sets of t symmetrically equivalent trajectories, where each trajectory in a set orbits about one of the stationary points. All trajectories in a set have the same energy, and consequently each set of trajectories corresponds to an t-fold degenerate energy cluster for the rotating molecule.

For a rigid asymmetric rotor the highest possible t value is 2, in accordance

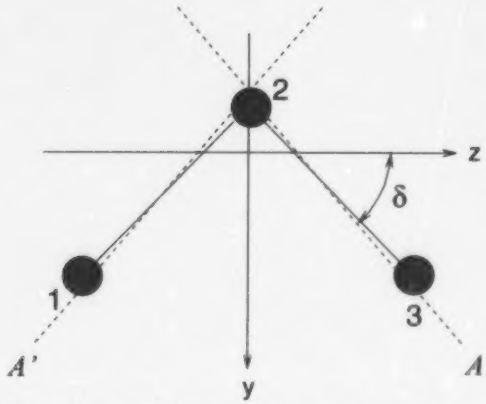

Fig. 15-16. The numbering of the nuclei and the molecule fixed axes (x, y, z) used for the H_2Te molecule. The x axis is perpendicular to the plane of the molecule and is defined so that the (x, y, z) axes form a right-handed coordinate system. The figure also shows the two stable rotation axes A and A' (see text).

with the twofold energy clusters in Fig. 15-15. As J is increased the shape of the RES of a rigid rotor hardly changes and the successive RES can be nested like Russian dolls. However, the introduction of centrifugal distortion into the calculation of the RES can lead to drastic changes. As in the methane example studied by Dorney and Watson (1972) the centrifugal rigidity about different molecule fixed axis directions in H_2Te is not constant, and at higher J the RES will "dimple-in" in directions of high centrifugal nonrigidity; relative to this there will be a "ballooning-out" in directions of centrifugal rigidity. This is simply because the rotational energy depends on the reciprocal of the instantaneous moment of inertia and the instantaneous moment of inertia is increased more when there is rotation around axes about which there is greater centrifugal nonrigidity.

Makarewicz (1990) has studied the RES of a triatomic molecule that is allowed to bend under the effect of the centrifugal forces of rotation, but for which the bond lengths are kept fixed. As J increases a dramatic change in the structure of the RES takes place at the so-called critical J-value J_{crit}. For $J < J_{\text{crit}}$ the RES of the rigid-bender molecule is similar to that of the corresponding rigid rotor, so that it has stationary points (maxima) in the $\pm z$ directions. For $J > J_{\text{crit}}$ these maxima are replaced by saddle points, and four new symmetrically equivalent maxima are formed in the yz plane (i.e., the molecular plane; see Fig. 15-16). The directions to the four stationary points are given by the axes A and A' in the figure. As shown in Fig. 15-16 the axes A and A' are at angles $\pm\delta$ with the molecule fixed z axis. The angle δ ($\approx 45°$) is slightly J dependent. Each of the two axes almost coincides with a Te-H bond.

For $J > J_{\text{crit}}$ the maximum energy on the RES is at the four new symmetrically equivalent stationary points, and nearly fourfold degenerate energy

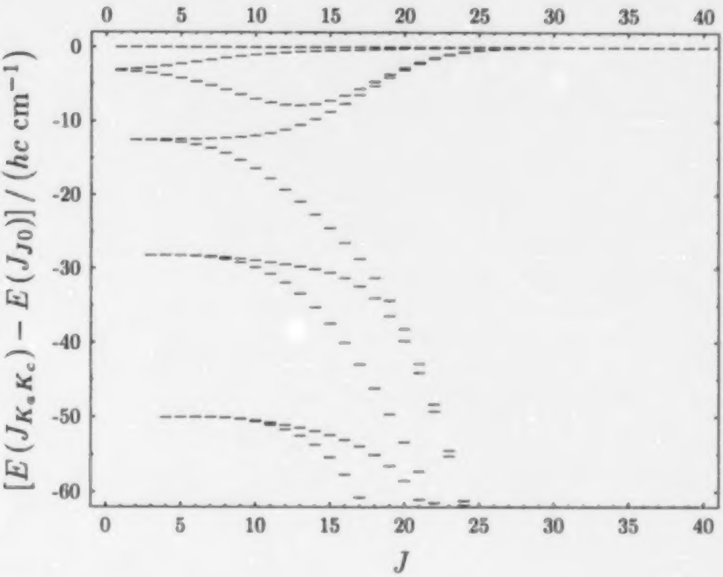

Fig. 15-17. The rotational energy level structure in the vibrational ground state of the $H_2{}^{130}Te$ molecule, calculated with the MORBID program (see Section 15.4.7) from the potential energy surface determined by Gómez and Jensen (1997) by fitting to experimental data. The term values are plotted relative to the highest term value for each J multiplet.

clusters emerge. The components of the fourfold energy cluster correspond to the set of four smallest possible, symmetrically equivalent, trajectories of $\mathbf{J}$ around the four stationary points. That is, in the highest energy levels for a given J value, the angular momentum vector lies essentially along either the A or the A' axis in Fig. 15-16. In classical theory the angular momentum vector is conserved in time and so, during the classical rotation of the molecule, the direction of one of the axes A or A' relative to a space-fixed axis system remains fixed. Hence we can say that the molecule rotates around this axis. It is easy to appreciate that if the bond angle is 90° then in the rigid-bender model there is complete centrifugal rigidity if the molecule rotates about either of the bonds. This will lead to a relative ballooning-out of the RES in these directions. There are two of these centrifugally rigid axes (A and A') and the molecule can rotate in two directions about each. Hence we get fourfold energy clusters. In Fig. 15-17, we show a part of the rotational energy level structure in the vibrational ground state of $H_2{}^{130}Te$, calculated using the MORBID program (see Section 15.4.7) from the potential energy surface determined by Gómez and Jensen (1997) by fitting to experimental data. The calculation now allows for stretching centrifugal distortion but this makes no qualitative change.

The energy level structure in Fig. 15-17 is very different from that of the rigid rotor shown in Fig. 15-15 in that the four highest energies for each J value [with $(K_a, K_c) = (J, 0)$, $(J, 1)$, $(J-1, 1)$, and $(J-1, 2)$, respectively] form fourfold clusters as predicted by the RES theory taking into account vibrational motion. The MORBID results agree well with term values derived from experimental data [see Gómez and Jensen (1997)]. For $H_2{}^{130}Te$, the term values with $K_a = J$ and $J-1$ in each J multiplet of the vibrational ground state have been determined experimentally for $J \leq 16$ [Kozin, Jensen, Polanz, Klee, Poteau, and Demaison (1996)].

The formation of fourfold energy clusters was first experimentally verified for the vibrational ground state of $H_2{}^{80}Se$[16] by Kozin, Belov, Polyansky, and Tretyakov (1992) and for the ν_1/ν_3 states of $H_2{}^{80}Se$ [where the clustering pattern is different from that in the vibrational ground state; see Lehmann (1991) and Kozin and Jensen (1993)] by Flaud, Camy-Peyret, Bürger, Jensen, and Kozin (1995). Further experimental studies are summarized by Jensen, Osmann, and Kozin (1997) [see also Gómez and Jensen (1997) and Gómez, Pacios, and Jensen (1997), and the references therein].

Simple semi-classical theory [see Kozin, Belov, Polyansky, and Tretyakov (1992)] predicts J_{crit}-values of 15 for $H_2{}^{32}S$, 12 for $H_2{}^{80}Se$, and 8 for $H_2{}^{130}Te$. For $H_2{}^{32}S$ [Kozin and Jensen (1994)] and $H_2{}^{80}Se$ [Jensen and Kozin (1993)], MORBID calculations have shown that at $J \approx J_{\mathrm{crit}}$, the energy separation between the two doublets at highest energy in the J multiplets of the vibrational ground state starts decreasing with increasing J. Hence we can say that for H_2S and H_2Se, the quantum mechanical MORBID calculations [whose results agree well with the available experimental data] confirm the values of J_{crit} obtained from semi-classical theory. For $H_2{}^{130}Te$, the low semi-classical value of J_{crit} suggested that clusters would appear at relatively low J values and thus be easily observable. This expectation was not confirmed by quantum mechanics since it could be shown, first in *ab initio* calculations [Jensen, Li, Hirsch, Buenker, Lee, and Kozin (1995)] and then experimentally [Kozin, Jensen, Polanz, Klee, Poteau, and Demaison (1996)], that the cluster formation in $H_2{}^{130}Te$ is very similar to that in $H_2{}^{80}Se$. Obviously the semi-classical theory does not correctly describe the rotational motion at J values as low as 8.

The rotation-vibration wavefunctions obtained from the MORBID calculations on H_2S, H_2Se, and H_2Te have been subjected to detailed analysis [see Jensen, Osmann, and Kozin (1997) and the references therein], and the results provide a quantum mechanical confirmation of the semi-classical description of the rotational motion at high J values. Specifically, the MORBID analysis shows that in the cluster states of highest energy in a J multiplet, the probability of the angular momentum having a projection of $J\hbar$ or $-J\hbar$ along one of the axes A or A' is very close to unity. Thus, to the extent allowed by quantum mechanics, the angular momentum is directed along the A or A' axis in these states, as predicted by the semi-classical theory. The MORBID results also demonstrate that in excited stretching vibrational states, the cluster formation is closely related to the onset of ***local mode behavior*** in the molecule. That is, in the cluster levels of these vibrational states, the vibrational excitation is localized in one of the H-X bonds.[17] Conventional local mode theory, which often neglects molecular rotation entirely, expects the local mode localization to be brought about by vibrational excitation so that it will be found for highly excited stretching states only. In the case of cluster formation, the local mode behavior arises through rotation-vibration interaction so that, in a sense, it is caused by rotational excitation.

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[16] In this case, the term values with $K_a = J$ and $J-1$ have been derived from experiment for $J \leq 23$ [Kozin, Belov, Polyansky, and Tretyakov (1992); Kozin, Klee, Jensen, Polyansky, and Pavlichenkov (1993)]. MORBID calculations [Jensen and Kozin (1993)] reproduce well the experimentally derived term values.

Zhilinskii and Pavlichenkov (1988) [see, also, Pavlichenkov and Zhilinskii (1988)] were the first to point out that at high J values, the rotational energy levels of an H_2X molecule form fourfold clusters. They reached this conclusion in a purely classical study which neglected the stretching vibrations. Their calculations were carried out for H_2O, and it is ironic that so far, energy clusters have not been identified for this molecule, either experimentally or in realistic quantum mechanical calculations. The work of Kozin and Pavlichenkov (1996) strongly suggests a reason for this. These authors calculated J_{crit} for the vibrational ground state of $H_2{}^{16}O$ in a classical model that accounts only for the bending motion of the molecule [i.e., a rigid bender model analogous to that used by Zhilinskii and Pavlichenkov (1988)], and in a classical model that takes into account all vibrational motions of the molecule. For the rigid bender model, they obtained $J_{\text{crit}} = 27$, but for the 'complete' model, they obtained $J_{\text{crit}} = 36$. The analogous displacements for H_2S, H_2Se, and H_2Te were all less than 2. Obviously the cluster formation in the vibrational ground state of H_2O is very strongly influenced by the stretching vibrational motion. This influence, which was not accounted for in the work of Zhilinskii and Pavlichenkov (1988), produces a J_{crit} value so large that if fourfold clusters form in H_2O, they will appear at J-values so high that the corresponding rotational energies are not easily obtained in spectroscopic experiments or in precise quantum mechanical calculations.

The clustering pattern of the energy levels of heavy spherical top molecules such as CF_4 and SF_6 have been the subject of much experimental and theoretical study [see Harter and Patterson (1984) and Brodersen and Zhilinskii (1995), and the papers to which they refer].

For the H_2X molecules studied here, the MS group (which is equal to the CNPI group) is $\boldsymbol{C}_{2v}(M)$ [see Table A-5]. For the molecules H_2S, H_2Se, and H_2Te, MORBID calculations [see Jensen, Osmann, and Kozin (1997) and references therein] have shown that the rotation-vibration wavefunctions corresponding the fourfold energy clusters formed at high J and K_a values have the MS group symmetry $A_1 \oplus A_2 \oplus B_1 \oplus B_2$. As discussed above, according to classical arguments the four components of each cluster represent the molecule rotating either about the A axis [which almost coincides with the Te-H_3 bond; see Fig. 15-16] or the A' axis [which almost coincides with the Te-H_1 bond] in either a right-handed or left handed sense; an obvious notation for these four states is 1R, 1L, 3R and 3L. The cluster states represent the four stationary points on the rotational energy surface, and for sufficiently high values of J and K_a the molecules (or equivalently the rotation-vibration wavefunctions) become localized at one of these points. This is exactly analogous to the localization described in Section 3.3 for the wavefunctions of a molecule with multiple equivalent minima on the potential energy surface.

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[17] See, for example, Mills and Robiette (1985) for a discussion of local mode theory.

In Chapter 3 criteria for determining whether an element of the CNPI group of a molecule is feasible were given. When we only consider a molecule in a single electronic state this criterion depends on whether energy level clusters arising from the localization of states in equivalent potential energy minima are resolved. (We have reworded the criterion given in Chapter 3 in order to draw a parallel with the clustering discussed in the present section.) The clustering discussed in Chapter 3 can be called "potential energy clustering" whereas that discussed in this section is "kinetic-energy clustering." We are now led naturally to the definition of another criterion for feasibility that is to be used if such kinetic-energy clusters are unresolved, and when we do not wish to label the individual components of such a cluster. This new criterion can be phrased as follows: An element of the CNPI group is unfeasible if it interconverts wavefunctions that are localized on the rotational energy surface and if the resultant cluster is unresolved at the experimental resolution being used [see Jensen and Bunker (1994)].

In the case of an H_2X molecule in a state with high J and K_a the new definition means that the operation (13) (which interconverts 1R with 3R and 1L with 3L), the operation E^* (which interconverts 1R with 1L and 3R with 3L), and the operation $(13)^*$ (which interconverts 1R with 3L and 1L with 3R) are all unfeasible. The MS group becomes $\boldsymbol{G}_1 = \{E\}$. The clustered energy levels are non-degenerate in $\boldsymbol{G}_1$.

If we apply the idea of the reverse correlation table [Section 5.9] to the group $\boldsymbol{C}_{2v}(M)$ and its subgroup $\boldsymbol{G}_1$, it follows unambiguously that the four wavefunctions representing the states in an unresolved fourfold degenerate rotational cluster must necessarily span the reducible representation $A_1 \oplus A_2 \oplus B_1 \oplus B_2$ in $\boldsymbol{C}_{2v}(M)$. This confirms the conclusions drawn from the results of MORBID calculations [see Jensen, Osmann, and Kozin (1997) and references therein].

BIBLIOGRAPHICAL NOTES

Hougen and DeKoven (1983) discuss the application of EMS groups to the classification of the rotation-torsion states of molecules containing a symmetric rotor attached to an asymmetric rotor.

Kręglewski (1978,1989,1993) has considered methylamine (CH_3NH_2) which has two contortional coordinates (inversion and internal rotation). The MS group of inverting and internally-rotating methylamine is G_{12} (see Table A-24), the same as nitromethane. It would be best if the same notation for the irreducible representations were used for both molecules.

Lodyga, Kręglewski and Makarewicz (1997) have considered hydrazine which has three contortional coordinates (two inversions and internal rotation). The MS group of this molecule was discussed by Longuet-Higgins (1963); it is the group G_{16} (see Table A-25) as for ethylene or the water dimer.

The effective Hamiltonian approach

Achieving a fitting of the rotation-contortion-vibration energy levels that is at the level of the experimental precision is very difficult, but Hougen and coworkers have developed effective Hamiltonians that allow this [see, for example, Tsunekawa, Kojima and Hougen (1982), Ohashi, Takagi, Hougen, Olson and Lafferty (1987), Ohashi, Tsunekawa, Takagi and Hougen (1989), Coudert and Hougen (1990), and Xu and Hougen (1995)].

Cordonnier and Coudert (1996) have developed the so-called internal axis method like (IAM like) formalism, which is an effective Hamiltonian matrix method originally set up by Hougen (1985) for the water dimer, to analyze the microwave spectrum of the nonrigid molecular ion $C_2H_3^+$. This method can be applied to any nonrigid molecule and is capable of achieving results, i.e., the calculation of the magnitude of the contortional splittings including their variation with rotational state, that are at the level of experimental precision.

Groner (1997) discusses the development of an effective rotational Hamiltonian for the purpose of fitting ground contortional-vibrational energies of molecules having two contortional motions.

Methanol

There is an enormous literature on methanol and some of the papers are listed below. The system used for labeling the torsional energy levels stems from before the MS group was introduced.

Koehler and Dennison (1940).
Burkhard and Dennison (1951).
Ivash and Dennison (1953).
Hecht and Dennison (1957).
Lin and Swalen (1959).
Kirtman (1962).
Lees and Baker (1968)
Kwan and Dennison (1972).
Herbst, Messer, De Lucia, and Helminger (1984).
Anderson, Herbst, and De Lucia (1992).
Tang and Takagi (1993).
Hougen, Kleiner, and Godefroid (1994).
Xu and Hougen (1995a).
Xu and Hougen (1995b).
Odashima, Matsushima, Nagai, Tsunekawa, and Takagi (1995).
Xu and Lovas (1997).
Hougen (1997).

16

Weakly Bound Cluster Molecules

Weakly bound cluster molecules form a special class of nonrigid molecule and they require special discussion. We give a general derivation of the rotation-contortion-vibration Hamiltonian of a dimer using both space fixed and body fixed axis systems. We also give general derivations of the dipole moment expansions that lead to the optical selection rules for both these cases. It is very appropriate for molecules of this type to use irreducible spherical tensor notation in the derivations. The hydrogen and ammonia dimers are used as examples.

16.1 INTRODUCTION

The study of weakly bound cluster molecules (see page 43) is a large field of research and we give a review here. The reader is referred to the papers mentioned in the text below, and to those given in the Bibliographical Notes for more details.

We use the same notation of 'contortional' coordinates for weakly bound cluster molecules as we have used in Chapter 15. The contortional coordinates are the intermoiety distances (and angles) required to specify the relative locations of the moiety centers of mass, and the angles specifying the relative orientations of the moieties. As an example, a trimer consisting of three nonlinear moieties has 12 contortional coordinates and the rotation-contortion Hamiltonian has 15 degrees of freedom. In exceptional cases, for example involving moieties such as NH_3 and CH_3OH, one or more moiety coordinates might be included as a contortional coordinate. If one or more of the moieties is linear, or an atom, there will be fewer contortional degrees of freedom. The multi-dimensional rotation-contortion Hamiltonian can be written as in Eq. (15-5), generalized to include many contortional coordinates, and depending on the convention used for locating (or embedding) the molecule fixed axes (more generally called the body fixed axes when we do not use the Eckart conditions to locate them) in the molecule the kinetic energy operator takes on different forms. The choice of how to locate the body fixed axes is part of the general process of choosing the coordinates for expressing the Hamiltonian, and this is the first stage in developing the optimum strategy for calculating the energy levels. As usual the coordinates are chosen with an eye to obtaining a zero order Hamiltonian that is (ideally) appropriate, separable and tractable with minimum approximation. In general, the coordinate choice we make is mainly governed by the nature and strength of the dependence of the intermoiety potential on the contortional (particularly angular) degrees of freedom. We also have to consider how easy it is to express the kinetic and potential energies in the chosen coordinates, and how easy it is to solve the resultant Schrödinger equation.

The main reason for studying weakly bound clusters is to determine the potential energy functions, and thereby to achieve a greater understanding of the intermolecular forces that hold such clusters together. The forces can be calculated from the slopes of the intermolecular potential (the force is given by $F = -\partial V/\partial R$ in one dimension). These forces are also responsible for the interaction between molecules in liquids and solids, and so the study of increasingly larger clusters will lead to a better understanding of the condensed phase. A recent book [Stone (1996)] is devoted entirely to the subject of intermolecular forces, and a detailed account is out of place here. However, it should be realized that the use of highly correlated *ab initio* methods with large well balanced basis sets (see Section 9.4) can lead to very accurate potentials for dimers. Such calculations fall into two categories: Supermolecule calculations using many-body perturbation theory (MBPT) based on the Møller-Plesset partitioning of the Hamiltonian [see, for example, Chałasiński and Szczęśniak (1994)], and the symmetry-adapted perturbation theory (SAPT) method in which one calculates directly the interaction energy between the moieties [see, for example, Jeziorski, Moszyński and Szalewicz (1994)]. Calculations at such a high level of *ab initio* theory are not usually practical for larger clusters and some elements of modeling, together with some limitations in the number of contortional coordinates that are allowed to vary, have to be introduced. For the water trimer, for example, such limited dimensionality *ab initio* calculations by Bürgi, Graf, Leutwyler and Klopper (1995), and by van Duijneveldt-van de Rijdt and van Duijneveldt (1995), have proved very useful, when combined with some semiempirical modeling, in analyzing the high resolution spectrum [see van der Avoird, Olthof, and Wormer (1996) and Olthof, van der Avoird, Wormer, Liu and Saykally (1996) and references therein]. The MS group of the water trimer $(H_2O)_3$ or $(D_2O)_3$ is discussed in van der Avoird, Olthof, and Wormer (1996); it is a group of 48 elements. The group is not isomorphic to the CNPI group $\boldsymbol{G}_{48}$ of CH_4 (see Table A-29); it has separably degenerate irreducible representations. The group is the direct product of $\{E, E^*\}$ and a pure permutation group of order 24 that is isomorphic to the point group $\boldsymbol{T}_h$.

16.2 THE HAMILTONIAN

The simplest limiting case is that in which the intermoiety potential does not depend on the relative angular orientations of the moieties. Such an intermoiety potential is isotropic and it is like the limiting case of the free internal rotor model for a torsional potential. For a dimer in this limiting case the rotation-contortion-vibration coordinates are the Euler angles (three for a nonlinear moiety, two for a linear moiety and none for an atom moiety) of the two moiety fixed axis systems, the vibrational normal coordinates Q_{r_A} and Q_{r_B} of the moieties [where $r_A = 1, 2, \ldots 3N_A - 6$ and $r_B = 1, 2, \ldots 3N_B - 6$ for nonlinear moieties containing N_A and N_B nuclei respectively], and the coordinates R, θ and ϕ that specify the length and spatial orientation of the intermoiety vector $\boldsymbol{R}$. In using these coordinates we refer the moiety orientations, and the intermoiety vector, to the space fixed axis system, and as a result the Hamiltonian obtained is said to involve using a 'space fixed reference frame'. This form for the rotation-contortion Hamiltonian for a dimer was initially used for the calculation of molecule-molecule scattering cross sections using the close-coupling method [see Arthurs and Dalgarno (1960) and Green (1975)], but the bound states of the Hamiltonian can also be calculated [see, for example, Hutson (1991)].

An important fact about the space fixed reference frame Hamiltonian is that it does not separate into rotation and contortion-vibration parts. Such a separation is often desirable in zero order and is achieved by introducing a set of body fixed (x, y, z) axes. This leads to the 'body fixed reference frame' Hamiltonian. When the anisotropy of the potential is large compared to the rotational constants of the molecule one can still express the potential in the space fixed reference frame coordinates, but it is more natural and straightforward to express it in terms of the angles that relate the orientations of the moieties to the intermoiety bonds, and such coordinates will naturally occur if we use a body fixed axis system. The price we pay for using coordinates that simplify the potential energy is, of course, increased complexity in the derivation of, and expression for, the kinetic energy. A comparison of space fixed and body fixed formalisms for calculating scattering cross sections is given by Pack (1974). He shows that the space fixed formalism is simpler and computationally faster for large values of the angular momentum J in distant collisions, whereas the body fixed formalism is simpler and computationally faster for low J values in short-range collisions. Thus, we expect the body fixed Hamiltonian to be more appropriate for the calculation of the bound states of a weakly bound cluster molecule having a significantly anisotropic potential unless J is high.

16.2.1 The space fixed reference frame Hamiltonian

The space fixed reference frame Hamiltonian for the dimer AB is

$$\hat{H}_{\mathrm{rcv}}{}^{(s)} = \hat{H}_{\mathrm{moieties}} + \hat{T}_{\mathrm{int}}{}^{(s)} + \hat{V}_{\mathrm{int}}{}^{(s)}, \tag{16-1}$$

where $\hat{H}_{\mathrm{moieties}}$ is the sum of the rotation-vibration Hamiltonians of the moieties, given by

$$\hat{H}_{\mathrm{moieties}} = \hat{H}_{\mathrm{rv}}(\mathrm{A}) + \hat{H}_{\mathrm{rv}}(\mathrm{B}). \tag{16-2}$$

and

$$T_{\mathrm{int}}^{(0)} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{1}{2\mu R^2}\boldsymbol{l}^2, \tag{16-3}$$

where

$$\mu = M_{\mathrm{A}}M_{\mathrm{B}}/(M_{\mathrm{A}} + M_{\mathrm{A}}), \tag{16-4}$$

is the dimer reduced mass (M_{A} and M_{B} are the moiety masses), and $\boldsymbol{l}$ is the end-over-end angular momentum operator of the moiety centers of mass. In this space fixed reference frame the moiety Euler angles are $(\theta_{\mathrm{A}},\phi_{\mathrm{A}},\chi_{\mathrm{A}})$ and $(\theta_{\mathrm{B}},\phi_{\mathrm{B}},\chi_{\mathrm{B}})$, and the space fixed Euler angles specifying the orientation of the intermoiety bond are (θ,ϕ). We can expand the space fixed intermoiety potential energy (including the coupling of the moiety normal coordinates with R) as a function of these eight Euler angles by writing it as the product of three rotation functions $D^{(j)*}_{nk}$ [see Eqs. (11-13)-(11-19)]. We do this to facilitate the calculation of the matrix elements of $V_{\mathrm{int}}^{(\mathrm{s})}$ in a basis set involving symmetric top functions $|j_{\mathrm{A}},k_{\mathrm{A}},m_{\mathrm{A}}\rangle$, $|j_{\mathrm{B}},k_{\mathrm{B}},m_{\mathrm{B}}\rangle$ and $|l,0,m_l\rangle$ depending on the three sets of Euler angles $(\theta_{\mathrm{A}},\phi_{\mathrm{A}},\chi_{\mathrm{A}})$, $(\theta_{\mathrm{B}},\phi_{\mathrm{B}},\chi_{\mathrm{B}})$ and $(\theta,\phi,0)$ respectively. The matrix elements of $D^{(j)*}_{mk}$ functions between symmetric top wavefunctions are straightforwardly obtained from Eq. (14-23). Since $V_{\mathrm{int}}^{(\mathrm{s})}$ is a scalar the expansion used must transform according to the totally symmetric representation $D^{(0)}$ of $\boldsymbol{K}$(spatial). We obtain such an expansion by coupling the $D^{(j)*}_{mk}$ functions using Eq. (10-98) twice. Once with $(N,S,J) = (\lambda_{\mathrm{A}},\lambda_{\mathrm{B}},\lambda_{\mathrm{AB}})$, and a second time (remembering that the potential is a scalar) with $(N,S,J) = (\lambda_{\mathrm{AB}},\lambda_{\mathrm{R}},0)$ $= (\lambda_{\mathrm{R}},\lambda_{\mathrm{R}},0)$. Making use of the identity

$$\begin{pmatrix} \lambda_{\mathrm{R}} & \lambda_{\mathrm{R}} & 0 \\ m_{\mathrm{R}} & -m_{\mathrm{R}} & 0 \end{pmatrix} = (-1)^{\lambda_{\mathrm{R}}-m_{\mathrm{R}}}(2\lambda_{\mathrm{R}}+1)^{-1/2}, \tag{16-5}$$

we obtain the appropriate expression having $D^{(0)}$ symmetry in $\boldsymbol{K}$(spatial) as

$$\begin{aligned} V_{\mathrm{int}}^{(\mathrm{s})} = \sum_{\Omega} V_{\Omega}(R,Q_{r_{\mathrm{A}}},Q_{r_{\mathrm{B}}}) \sum_{m_{\mathrm{A}},m_{\mathrm{B}},m} \begin{pmatrix} \lambda_{\mathrm{A}} & \lambda_{\mathrm{B}} & \lambda_{\mathrm{R}} \\ m_{\mathrm{A}} & m_{\mathrm{B}} & m_{\mathrm{R}} \end{pmatrix} \\ \times [D^{(\lambda_{\mathrm{A}})}_{m_{\mathrm{A}}k_{\mathrm{A}}}(\phi_{\mathrm{A}},\theta_{\mathrm{A}},\chi_{\mathrm{A}})]^*[D^{(\lambda_{\mathrm{B}})}_{m_{\mathrm{B}}k_{\mathrm{B}}}(\phi_{\mathrm{B}},\theta_{\mathrm{B}},\chi_{\mathrm{B}})]^*[D^{(\lambda_{\mathrm{R}})}_{m_{\mathrm{R}}0}(\phi,\theta,0)]^*, \end{aligned} \tag{16-6}$$

where $\Omega = \lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{R}}k_{\mathrm{A}}k_{\mathrm{B}}$, and the sum is truncated once the $V_{\Omega}(R,Q_{r_{\mathrm{A}}},Q_{r_{\mathrm{B}}})$ have become sufficiently small. If moiety A is linear k_{A} and χ_{A} disappear, and if moiety B is linear k_{B} and χ_{B} disappear. A factor $(-1)^{\lambda_{\mathrm{A}}-\lambda_{\mathrm{B}}+\lambda_{\mathrm{R}}}$ [obtained from using Eq. (10-98) twice] has been absorbed into the V_{Ω} coefficient. Other expansions of the potential are possible but this functional form ensures completeness, and with it the angular matrix elements are straightforward to determine. The coefficients $V_{\Omega}(R,Q_{r_{\mathrm{A}}},Q_{r_{\mathrm{B}}})$ are appropriately chosen analytical functions of R, $Q_{r_{\mathrm{A}}}$ and $Q_{r_{\mathrm{B}}}$ involving parameters that are either modeled or that are determined by fitting to *ab initio* or other theoretical values for the contortional potential energy. The $V_\Omega(R,Q_{r_A},Q_{r_B})$ coefficients will be restricted by the fact that $V_{\text{int}}^{(s)}$ has to be totally symmetric in the MS group. For an isotropic potential, with no coupling of the moiety coordinates with R, the eigenfunctions of this Hamiltonian are 'free-rotor' products [see Eqs. (16-32)-(16-34) below] of the rotation-vibration wavefunctions of each moiety times the rotation-vibration eigenfunctions of $\hat{H}_{\text{int}}{}^{(s)}$ (= $\hat{T}_{\text{int}}{}^{(s)} + V_{\text{int}}{}^{(s)}$), and the energies are simply the sum of the eigenvalues of $\hat{H}_{\text{int}}{}^{(s)}$ built on the rotation-vibration energies of the moieties. The eigenfunctions and eigenvalues of $\hat{H}_{\text{int}}{}^{(s)}$ when the potential is isotropic are like the rotation-vibration eigenfunctions and eigenvalues of a diatomic molecule; in particular the zero order rotational energies will be given (in cm^{-1}) by $Bl(l+1)$ where B is the expectation value of $\hbar^2/(2\mu R^2hc)$ and l is the end-over-end rotational quantum number.

In practice the potential usually depends very significantly on the orientations of the moieties with respect to the intermoiety bond, but very weak anisotropy (relative to the end-over-end rotational constant B) does occur in a few dimers including the important case of the H_2 dimer. This form of the Hamiltonian with an isotropic potential function does provide us with an important limiting case for which we can easily appreciate the rotation-contortion-vibration energy level pattern and symmetry labels. For a weakly bound cluster molecule that contains more than two moieties the zero order isotropic space fixed reference frame Hamiltonian $\hat{H}_{\text{rcv}}{}^{(s)}$ will be as in Eq. (16-1) but $\hat{H}_{\text{moieties}}$ will involve the sum of the the rotation-vibration Hamiltonians of all the moieties, and $\hat{T}_{\text{int}}{}^{(s)}$ will be the rotation-vibration kinetic energy operator involving the motions of all the centers of mass of the moieties. In this limiting case the isotropic molecular cluster potential energy function would not depend on the angular orientations of the moieties.

16.2.2 The body fixed reference frame Hamiltonian

The body fixed reference frame rotation-contortion-vibration Hamiltonian is set up for a dimer by using body fixed (x,y,z) axes with origin at the nuclear center of mass, with z axis directed along the line pointing from the center of mass of moiety A to that of moiety B (which specifies the Euler angles θ and ϕ), and with xy axes oriented so that the Euler angle χ is 0. The derivation of the Hamiltonian is identical to that given in Eqs. (17-12)-(17-40) for the rovibronic Hamiltonian of a diatomic molecule, except in that derivation the (x,y,z) coordinates of the electrons should be replaced by the (x,y,z) coordinates of the moiety nuclei. As a result the electronic kinetic energy [Eq. (17-38)] should be replaced by $\hat{H}_{\text{moieties}}$, and the electronic angular momentum $\hat{\boldsymbol{L}}$ in the (x,y,z) axis system [Eq. (17-20)] should be replaced by the angular momentum

$$\hat{\jmath} = \hat{\jmath}_A + \hat{\jmath}_B \tag{16-7}$$

of the moiety nuclei in the (x,y,z) axis system. The derivation uses the Method I technique for changing coordinates in a Hamiltonian, i.e., it uses the chain rule rather than the Podolsky trick (see Section 9.2). The rotation-contortion-vibration Hamiltonian obtained [see Eqs. (17-38)-(17-40)] is

$$\hat{H}_{\mathrm{rcv}}{}^{(\mathrm{m})} = \hat{H}_{\mathrm{moieties}} + \hat{T}_{\mathrm{int}}{}^{(\mathrm{m})} + V_{\mathrm{int}}{}^{(\mathrm{m})}, \tag{16-8}$$

where

$$\begin{aligned} \hat{T}_{\mathrm{int}}{}^{(\mathrm{m})} = & -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) \\ & + \frac{1}{2\mu R^2}\left[(\hat{J}_x - \hat{j}_x)^2 + \frac{1}{\sin\theta}(\hat{J}_y - \hat{j}_y)\sin\theta(\hat{J}_y - \hat{j}_y)\right]. \end{aligned} \tag{16-9}$$

The potential $V_{\mathrm{int}}{}^{(\mathrm{m})}$ is a function of R, $Q_{r_{\mathrm{A}}}$ and $Q_{r_{\mathrm{B}}}$, a function of the angles specifying the orientations of the moieties with respect to the intermoiety bond, and a function of the torsional angle between the moieties (six coordinates in the case of two nonlinear moieties). It is not a function of the Euler angles of the (x, y, z) axis system, and so it involves three variables less than $V_{\mathrm{int}}{}^{(\mathrm{s})}$. It is the natural coordinate system in which an *ab initio* potential energy function would be determined. We discuss the potential $V_{\mathrm{int}}{}^{(\mathrm{m})}$ further below. The expression for $\hat{T}_{\mathrm{int}}{}^{(\mathrm{m})}$ given above is derived by Brocks, van der Avoird, Sutcliffe and Tennyson (1983), and by van der Avoird, Wormer and Moszynski (1994).

In Eq. (16-9) the (x, y, z) components of the total angular momentum $\boldsymbol{J}$, and of the internal moiety angular momentum $\boldsymbol{j}$, satisfy the commutation relations given in Eqs. (17-27)-(17-29) and Eqs. (17-31)-(17-36) (where $\hat{\boldsymbol{L}}$ should be replaced by $\boldsymbol{j}$). As a result of the absence of χ as a rotational variable we see that $\hat{H}_{\mathrm{int}}{}^{(\mathrm{m})}$ contains awkward $\sin\theta$ angular factors, and that the commutation relations of the (x, y, z) components of the angular momentum operators are complicated. Also the matrix elements involving these operator components in the rotational eigenfunctions are not the standard ones as given in Table 11-1. In Chapter 17, which focuses on linear molecules, it is shown how these problems are overcome by introducing Hougen's isomorphic Hamiltonian [Hougen (1962a)]. We do this here by introducing $\hat{\boldsymbol{J}}'$ and $\boldsymbol{j}'$ referred to an $x'y'z'$ axis system having Euler angles (ϕ, θ, χ) instead of $\boldsymbol{J}$ and $\boldsymbol{j}$ that are referred to the (x, y, z) axis system having Euler angles $(\phi, \theta, 0)$, and by restricting the basis functions used to diagonalize this Hamiltonian to be such that they have eigenvalue zero for $(\hat{J}_z - \hat{j}_z)$. In this way the angle χ is introduced as a variable, which simplifies the treatment, and we restrict the calculation so that only 'real' states are calculated. The reader should refer to Section 17.4 for more details. The isomorphic body fixed rotation-contortion-vibration Hamiltonian for a dimer is

$$\hat{H}_{\mathrm{rcv}}^{\mathrm{iso(m)}} = \hat{H}_{\mathrm{moieties}} + \hat{T}_{\mathrm{int}}^{\mathrm{iso(m)}} + V_{\mathrm{int}}{}^{(\mathrm{m})}, \tag{16-10}$$

where

$$\hat{T}_{\mathrm{int}}^{\mathrm{iso(m)}} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{1}{2\mu R^2}\left[(\hat{J}'_x - \hat{j}'_x)^2 + (\hat{J}'_y - \hat{j}'_y)^2\right], \tag{16-11}$$

and, as already stated, this is to be diagonalized in a basis having eigenvalue zero for $(J'_z - j'_z)$. The awkward looking $\sin\theta$ angular factors have disappeared from the Hamiltonian, the J'_α operators are the same as the J_α operators in Eqs. (10-84)-(10-86) and they commute with the j'_α operators. The j'_α have the same commutation relations as the j_α given in Eq. (17-36). The eigenvalue of J_z and j_z is $k\hbar$, and $K = |k|$ is a useful near quantum number label for the eigenstates. Coriolis coupling caused by the term $-[(1/(\mu R^2)](J'_x j'_x + J'_y j'_y)$ will mix states having different K values. For cluster molecules having more than two moieties the body fixed (x, y, z) axes would usually be located as principal axes of the moiety centers of mass frame, and we would not have the need to transform to an isomorphic Hamiltonian except if these centers of mass were colinear.

The expression for the intermoiety potential for a dimer AB in terms of the body fixed Euler angles $(\theta^{\rm m}_{\rm A}, \phi^{\rm m}_{\rm A}, \chi^{\rm m}_{\rm A})$ and $(\theta^{\rm m}_{\rm B}, \phi^{\rm m}_{\rm B}, \chi^{\rm m}_{\rm B})$ in the body fixed xyz axis system, is easily obtained from the expression for $V^{(\rm s)}_{\rm int}$ in the space fixed reference frame given in Eq. (16-6). We note that the $V_\Omega(R, Q_{r_{\rm A}}, Q_{r_{\rm B}})$ are unaffected by a rotation of axes, and that in the body fixed frame θ and ϕ becomes $\theta^{\rm m}$ and $\phi^{\rm m}$ which are both zero; the last $D^{(j)*}_{mk}$ function in $V^{(\rm s)}_{\rm int}$ becomes $[D^{(\lambda_{\rm R})}_{m_{\rm R}0}(0, 0, 0)]^*$ which is just $\delta_{0m_{\rm R}}$. Thus we obtain

$$V^{(\rm m)}_{\rm int} = \sum_{\Omega} V_\Omega(R, Q_{r_{\rm A}}, Q_{r_{\rm B}}) \sum_{m_{\rm A}} \begin{pmatrix} \lambda_{\rm A} & \lambda_{\rm B} & \lambda_{\rm R} \\ m_{\rm A} & m_{\rm B} & 0 \end{pmatrix} \times [D^{(\lambda_{\rm A})}_{m_{\rm A}k_{\rm A}}(\phi^{\rm m}_{\rm A}, \theta^{\rm m}_{\rm A}, \chi^{\rm m}_{\rm A})]^* [D^{(\lambda_{\rm B})}_{m_{\rm B}k_{\rm B}}(\phi^{\rm m}_{\rm B}, \theta^{\rm m}_{\rm B}, \chi^{\rm m}_{\rm B})]^*, \tag{16-12}$$

where $\Omega = \lambda_{\rm A}\lambda_{\rm B}\lambda_{\rm R}k_{\rm A}k_{\rm B}$ and $m_{\rm B} = -m_{\rm A}$. If moiety A is linear $k_{\rm A}$ and $\chi^{\rm m}_{\rm A}$ disappear, and if moiety B is linear $k_{\rm B}$ and $\chi^{\rm m}_{\rm B}$ disappear. The potential does not depend on the angle $\chi_A + \chi_B$, and as a result it will not mix basis functions having different values of the angular momentum quantum number K. The stronger is the anisotropy of the potential the more terms will be required in this expansion, and the larger the basis set required to achieve convergence. Thus at some point this expansion will be impractical to use. In this circumstance the molecule is heading in the direction of being a rigid molecule and other expansions of the potential, and other basis sets, will be more appropriate.

There are other ways that the body fixed (x, y, z) axes can be defined in a weakly bound cluster molecule. It can happen that one or more moieties in the cluster form a heavy rigid substructure around which the other moieties move more freely. In such a case the dynamics of the molecule is better approximated if we define the rotational variables by this rigid substructure. This means that the (x, y, z) axes would be located by reference to this substructure without regard for the location of the more freely moving moieties. A molecule of this type is the molecule CO@C_{60}, in which the CO moiety rather freely rotates *within* the C_{60} cage. Olthof, van der Avoird, and Wormer (1996) have made a theoretical study of this molecule and have predicted the infrared spectrum using the MS group I_h(M) given in Table A-16. Another problem can occur if one wants to include a moiety distortion (such as the inversion of the ammonia moieties in the ammonia dimer) as a contortion in the Hamiltonian. On the other hand one may want to restrict attention to just a few contortional coordinates in a complicated case and construct a rotation-contortion Hamiltonian of limited dimensionality. Such specialized Hamiltonians can be derived individually either by changing coordinates in the Cartesian coordinate representation of the quantum mechanical Hamiltonian using the chain rule (Method I), or by changing coordinates in the classical Hamiltonian in curvilinear coordinates using the Podolsky trick (Method II). The article by van der Avoird, Wormer and Moszynski (1994) reviews the various forms that the kinetic energy operator can take, and it has many references to other work in this area.

The Hamiltonian is set up above with inclusion of the coupling in the potential function of the vibrational coordinates of the moieties with the contortional coordinates. This occurs because the force constants of the moieties will in general be functions of the contortional coordinates, and it is allowed for by letting the V_Ω coefficients depend on the moiety normal coordinates. However, this coupling is usually very weak, as attested to by the fact that states in which the moiety vibrational energy greatly exceeds the dissociation energy of the intermoiety bond often exist with a long lifetime. The hydrogen dimer with an intermoiety dissociation energy (D_0) of only 3 cm^{-1} is an impressive example of this with sharp absorption spectra even at 8600 cm^{-1} [see Fig. 5 of McKellar (1990)]. A zero order treatment of the coupling between the contortional coordinates and the moiety vibrational coordinates involves the use of an effective contortional potential that depends on the vibrational states of the moieties, but more exact treatments are possible [see, for example, Qiu and Bačić (1997), and Qiu, Zhang, and Bačić (1998)].

16.3 THE DETERMINATION OF OPTICAL SELECTION RULES

To determine line strengths, and the selection rules, for allowed electric dipole transitions between rotation-contortion-vibration states of a weakly bound cluster molecule we begin by formally writing down the matrix elements of the components of the space fixed dipole moment operator $\mu_{\mathrm{s}}^{(1,\sigma)}$ [see Eq. (14-18)]. If a body fixed axis system is used to set up the wavefunctions we express $\mu_{\mathrm{s}}^{(1,\sigma)}$ in terms of the body fixed components $\mu_{\mathrm{m}}^{(1,\sigma')}$ [see Eq. (14-20)]. The $\mu_{\mathrm{m}}^{(1,\sigma')}$ would be expanded in the body fixed contortion-vibration coordinates and the matrix elements evaluated to determine line strengths, or used in order to determine selection rules. This is how one proceeds for rigid molecules, and for normal nonrigid molecules, when a body fixed axis system is used. However, if the wavefunctions are set up in the space fixed reference frame it is not appropriate to introduce $\mu_{\mathrm{m}}^{(1,\sigma')}$. In this case we expand $\mu_{\mathrm{s}}^{(1,\sigma)}$ in the space fixed coordinates and evaluate its matrix elements using the space fixed reference frame wavefunctions. We thus need to discuss the expansions of both $\mu_{\mathrm{s}}^{(1,\sigma)}$ in the space fixed coordinates, and $\mu_{\mathrm{m}}^{(1,\sigma)}$ in the body fixed coordinates.

For a dimer AB in the space fixed reference frame we expand $\mu_{\mathrm{s}}^{(1,\sigma)}$ as a function of the angles $(\theta_A, \phi_A, \chi_A, \theta_B, \phi_B, \chi_B, \theta, \phi)$ in the same way that we expand the dimer potential $V_{\rm int}^{(s)}$ in Eq. (16-6). Again, we aim at using Eq. (14-23) for calculating the integrals over the Euler angles. We again use three rotation functions $D_{mk}^{(j)*}$, and we again use Eq. (10-98) twice. But now the expansion has to transform as the representation $D^{(1)}$ of $\boldsymbol{K}$(spatial), rather than as $D^{(0)}$, because $\mu_{\rm s}^{(1,\sigma)}$ has $D^{(1)}$ symmetry. Because of this the expression does not simplify as much, and $\lambda_{\rm AB}$ runs from $|\lambda_{\rm A} - \lambda_{\rm B}|$ to $\lambda_{\rm A} + \lambda_{\rm B}$. We obtain

$$\begin{aligned}
\mu_{\rm s}^{(1,\sigma)} &= \sum_{\Lambda,\lambda_{\rm R}} \mu_{\Lambda,\lambda_{\rm R}}^{(s)}(R, Q_{r_{\rm A}}, Q_{r_{\rm B}}) \\
&\quad \times \sum_{\Gamma} (-1)^{\lambda_{\rm A}-\lambda_{\rm B}+\sigma_{\rm AB}} \sqrt{2\lambda_{\rm AB}+1} \begin{pmatrix} \lambda_{\rm A} & \lambda_{\rm B} & \lambda_{\rm AB} \\ \sigma_{\rm A} & \sigma_{\rm B} & -\sigma_{\rm AB} \end{pmatrix} \\
&\quad \times (-1)^{\lambda_{\rm AB}-\lambda_{\rm R}+\sigma} \sqrt{3} \begin{pmatrix} \lambda_{\rm AB} & \lambda_{\rm R} & 1 \\ \sigma_{\rm AB} & \sigma_{\rm R} & -\sigma \end{pmatrix} \\
&\quad \times [D_{\sigma_{\rm A}\sigma'_{\rm A}}^{(\lambda_{\rm A})}(\phi_{\rm A}, \theta_{\rm A}, \chi_{\rm A})]^* [D_{\sigma_{\rm B}\sigma'_{\rm B}}^{(\lambda_{\rm B})}(\phi_{\rm B}, \theta_{\rm B}, \chi_{\rm B})]^* [D_{\sigma_{\rm R}0}^{(\lambda_{\rm R})}(\phi, \theta, 0)]^*, \qquad (16\text{-}13)
\end{aligned}$$

where $\Lambda = \lambda_{\rm A}\lambda_{\rm B}\lambda_{\rm AB}\sigma'_{\rm A}\sigma'_{\rm B}$, and $\Gamma = \sigma_{\rm A}, \sigma_{\rm B}, \sigma_{\rm R}, \sigma_{\rm AB}$. If moiety A is linear $\sigma'_{\rm A}$ and $\chi_{\rm A}$ disappear, and if moiety B is linear $\sigma'_{\rm B}$ and $\chi_{\rm B}$ disappear. The expansion coefficients $\mu_{\Lambda,\lambda_{\rm R}}^{(s)}$ will be restricted by the symmetry Γ^* of $\mu_{\rm s}^{(1,\sigma)}$ in the MS group.

For a dimer AB in the body fixed reference frame we expand $\mu_{\rm m}^{(1,\sigma')}$ as a function of the angles $(\theta_{\rm A}^{\rm m}, \phi_{\rm A}^{\rm m}, \chi_{\rm A}^{\rm m})$ and $(\theta_{\rm B}^{\rm m}, \phi_{\rm B}^{\rm m}, \chi_{\rm B}^{\rm m})$, and we obtain the expression for $\mu_{\rm m}^{(1,\sigma')}$ by using the same arguments that led to Eq. (16-12). If we set $(\theta, \phi) = (\theta^{\rm m}, \phi^{\rm m}) = (0, 0)$ the body fixed axes will coincide with the space fixed axes so that in this special situation we have $\mu_{\rm m}^{(1,\sigma')} = \mu_{\rm s}^{(1,\sigma')}$. Making the substitution $[D_{m_{\rm R}0}^{(\lambda_{\rm R})}(0,0,0)]^* = \delta_{0m_{\rm R}}$ we derive

$$\begin{aligned}
\mu_{\rm m}^{(1,\sigma')} &= \sum_{\Lambda,\lambda_{\rm R}} \mu_{\Lambda,\lambda_{\rm R}}^{(s)}(R, Q_{r_{\rm A}}, Q_{r_{\rm B}}) \\
&\quad \times (-1)^{\lambda_{\rm A}-\lambda_{\rm B}+\sigma'} \sqrt{2\lambda_{\rm AB}+1} \sum_{\sigma_{\rm A},\sigma_{\rm B}} \begin{pmatrix} \lambda_{\rm A} & \lambda_{\rm B} & \lambda_{\rm AB} \\ \sigma_{\rm A} & \sigma_{\rm B} & -\sigma' \end{pmatrix} \\
&\quad \times (-1)^{\lambda_{\rm AB}-\lambda_{\rm R}+\sigma'} \sqrt{3} \begin{pmatrix} \lambda_{\rm AB} & \lambda_{\rm R} & 1 \\ \sigma' & 0 & -\sigma' \end{pmatrix} \\
&\quad \times [D_{\sigma_{\rm A}\sigma'_{\rm A}}^{(\lambda_{\rm A})}(\phi_{\rm A}^{\rm m}, \theta_{\rm A}^{\rm m}, \chi_{\rm A}^{\rm m})]^* [D_{\sigma_{\rm B}\sigma'_{\rm B}}^{(\lambda_{\rm B})}(\phi_{\rm B}^{\rm m}, \theta_{\rm B}^{\rm m}, \chi_{\rm B}^{\rm m})]^*. \qquad (16\text{-}14)
\end{aligned}$$

We have eliminated $\sigma_{\rm AB}$ from Eq. (16-14) since, for $\sigma_{\rm R} = 0$, the second $3j$-symbol in Eq. (16-13) will vanish unless $\sigma_{\rm AB} = \sigma$ ($= \sigma'$ here). If moiety A is linear $\sigma'_{\rm A}$ and $\chi_{\rm A}^{\rm m}$ disappear, and if moiety B is linear $\sigma'_{\rm B}$ and $\chi_{\rm B}^{\rm m}$ disappear. It follows from Eq. (14-15) that if we use $\chi = 0$ to define the body fixed axes,

$$\mu_{\rm s}^{(1,\sigma)} = \sum_{\sigma'=-1}^{1} \mu_{\rm m}^{(1,\sigma')} [D_{\sigma\sigma'}^{(1)}(\phi, \theta, 0)]^*. \qquad (16\text{-}15)$$

For a dimer with a $\chi = 0$ body fixed reference frame we use this equation to calculate line strengths, following the procedure discussed for rigid molecules in Chapter 14. If we were to use the isomorphic Hamiltonian of Eq. (16-10) then χ would not be set to zero in Eq. (16-15).

Equation (16-14) can be rewritten in the form

$$\begin{aligned} \mu_{\mathrm{m}}^{(1,\sigma')} &= \sum_{\Lambda} \mu_{\Lambda,\sigma'}^{(\mathrm{m})}(R, Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}}) \\ &\quad \times (-1)^{\lambda_{\mathrm{A}}-\lambda_{\mathrm{B}}+\sigma'} \sqrt{2\lambda_{\mathrm{AB}}+1} \sum_{\sigma_{\mathrm{A}},\sigma_{\mathrm{B}}} \begin{pmatrix} \lambda_{\mathrm{A}} & \lambda_{\mathrm{B}} & \lambda_{\mathrm{AB}} \\ \sigma_{\mathrm{A}} & \sigma_{\mathrm{B}} & -\sigma' \end{pmatrix} \\ &\quad \times [D_{\sigma_{\mathrm{A}}\sigma'_{\mathrm{A}}}^{(\lambda_{\mathrm{A}})}(\phi_{\mathrm{A}}^{\mathrm{m}}, \theta_{\mathrm{A}}^{\mathrm{m}}, \chi_{\mathrm{A}}^{\mathrm{m}})]^{*} [D_{\sigma_{\mathrm{B}}\sigma'_{\mathrm{B}}}^{(\lambda_{\mathrm{B}})}(\phi_{\mathrm{B}}^{\mathrm{m}}, \theta_{\mathrm{B}}^{\mathrm{m}}, \chi_{\mathrm{B}}^{\mathrm{m}})]^{*} \end{aligned} \tag{16-16}$$

with

$$\begin{aligned} \mu_{\Lambda,\sigma'}^{(\mathrm{m})}(R, Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}}) &= \sum_{\lambda_{\mathrm{R}}} \mu_{\Lambda,\lambda_{\mathrm{R}}}^{(\mathrm{s})}(R, Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}}) \\ &\quad \times (-1)^{\lambda_{\mathrm{AB}}-\lambda_{\mathrm{R}}+\sigma'} \sqrt{3} \begin{pmatrix} \lambda_{\mathrm{AB}} & \lambda_{\mathrm{R}} & 1 \\ \sigma' & 0 & -\sigma' \end{pmatrix}. \end{aligned} \tag{16-17}$$

If the dipole moment of the dimer were determined entirely by the free dipole moments of the two moieties, we could express the expansion function of Eq. (16-17) as

$$\begin{aligned} \mu_{\Lambda,\sigma'}^{(\mathrm{m})}(R, Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}}) &= \mu_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{A}}\sigma'_{\mathrm{B}},\sigma'}^{(\mathrm{m})}(Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}}) \\ &= \delta_{\lambda_{\mathrm{A}}1}\, \delta_{\lambda_{\mathrm{B}}0}\, \delta_{\sigma'_{\mathrm{B}}0}\, \mu_{\mathrm{m,A}}^{(1,\sigma'_{\mathrm{A}})}(Q_{r_{\mathrm{A}}}) \\ &\quad + \delta_{\lambda_{\mathrm{A}}0}\, \delta_{\lambda_{\mathrm{B}}1}\, \delta_{\sigma'_{\mathrm{A}}0}\, \mu_{\mathrm{m,B}}^{(1,\sigma'_{\mathrm{B}})}(Q_{r_{\mathrm{B}}}), \end{aligned} \tag{16-18}$$

where $\mu_{\mathrm{m,A}}^{(1,\sigma'_{\mathrm{A}})}(Q_{r_{\mathrm{A}}})$ and $\mu_{\mathrm{m,B}}^{(1,\sigma'_{\mathrm{B}})}(Q_{r_{\mathrm{B}}})$ are the irreducible spherical tensor operators representing the dipole moments for each of the moieties, expressed in the body fixed axis system of the respective moiety. We derive Eq. (16-18) by first using Eq. (14-15) to transform the dipole moment of each moiety to the body fixed reference frame of the dimer. These transformations involve the Euler angles $(\theta_{\mathrm{A}}^{\mathrm{m}}, \phi_{\mathrm{A}}^{\mathrm{m}}, \chi_{\mathrm{A}}^{\mathrm{m}})$ and $(\theta_{\mathrm{B}}^{\mathrm{m}}, \phi_{\mathrm{B}}^{\mathrm{m}}, \chi_{\mathrm{B}}^{\mathrm{m}})$, respectively. Then we add the two dipole moments and cast the resulting equation in the form of Eq. (16-16) by using the relation [see Eq. (2.30) of Zare (1988) and Eq. (16-5) here]

$$\begin{pmatrix} 1 & 0 & 1 \\ \sigma' & 0 & -\sigma' \end{pmatrix} = \begin{pmatrix} 0 & 1 & 1 \\ 0 & \sigma' & -\sigma' \end{pmatrix} = (-1)^{\sigma'+1}/\sqrt{3} \tag{16-19}$$

together with $[D_{00}^{(0)}(\theta_{\mathrm{A}}^{\mathrm{m}}, \phi_{\mathrm{A}}^{\mathrm{m}}, \chi_{\mathrm{A}}^{\mathrm{m}})]^{*} = [D_{00}^{(0)}(\theta_{\mathrm{B}}^{\mathrm{m}}, \phi_{\mathrm{B}}^{\mathrm{m}}, \chi_{\mathrm{B}}^{\mathrm{m}})]^{*} = 1$. Higher order corrections to $\mu_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}k_{\mathrm{A}}k_{\mathrm{B}},\sigma'}^{(\mathrm{m})}(Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}})$ are obtained if we consider the dipole moment on one moiety induced by the multipole moments of the other moiety. The dipole moment induced on moiety A by the free multipole moments on monomer B gives rise to the expansion coefficient given in Eq. (40) of van der Avoird, Wormer and Moszynski (1994):

$$\begin{aligned}
&\mu^{(\mathrm{m})}_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{A}}\sigma'_{\mathrm{B}},\sigma'}(R, Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}}) \\
&= \sum_{l_{\mathrm{A}}}(-1)^{\sigma'+l_{\mathrm{A}}}\sqrt{(2\lambda_{\mathrm{A}}+1)(2l_{\mathrm{A}}+2\lambda_{\mathrm{B}}+1)(2\lambda_{\mathrm{AB}}+1)} \\
&\times \begin{pmatrix} 2l_{\mathrm{A}}+2\lambda_{\mathrm{B}} \\ 2l_{\mathrm{A}} \end{pmatrix}^{1/2} \begin{pmatrix} l_{\mathrm{A}}+\lambda_{\mathrm{B}} & \lambda_{\mathrm{AB}} & 1 \\ 0 & \sigma' & -\sigma' \end{pmatrix} \\
&\times \begin{Bmatrix} l_{\mathrm{A}}+\lambda_{\mathrm{B}} & \lambda_{\mathrm{B}} & l_{\mathrm{A}} \\ \lambda_{\mathrm{A}} & 1 & \lambda_{\mathrm{AB}} \end{Bmatrix} \mu^{(\lambda_{\mathrm{B}},\sigma'_{\mathrm{B}})}_{\mathrm{m,B}}(Q_{r_{\mathrm{B}}})\,\alpha^{(1,l_{\mathrm{A}};\lambda_{\mathrm{A}},\sigma'_{\mathrm{A}})}_{\mathrm{m,A}}(Q_{r_{\mathrm{A}}})R^{-l_{\mathrm{A}}-\lambda_{\mathrm{B}}-1},
\end{aligned} \tag{16-20}$$

where the binomial coefficient

$$\begin{pmatrix} 2l_{\mathrm{A}}+2\lambda_{\mathrm{B}} \\ 2l_{\mathrm{A}} \end{pmatrix} = \frac{(2l_{\mathrm{A}}+2\lambda_{\mathrm{B}})!}{(2l_{\mathrm{A}})!\,(2\lambda_{\mathrm{B}})!}, \tag{16-21}$$

$\mu^{(\lambda_{\mathrm{B}},\sigma'_{\mathrm{B}})}_{\mathrm{m,B}}(Q_{r_{\mathrm{B}}})$ is component σ'_{B} of the irreducible spherical tensor operator representing the $2^{\lambda_{\mathrm{B}}}$-pole moment of moiety B, averaged over the electronic wavefunction for the electronic state occupied by the moiety [in a manner analogous to that described for the dipole moment operator in Eq. (14-27) for $\Phi^{(e',S',m'_S)}_{\mathrm{elec}} = \Phi^{(e'',S'',m''_S)}_{\mathrm{elec}}$], and the mixed dipole-$2^{l_{\mathrm{A}}}$-pole polarizability of moiety A is given by [see Eqs. (19), (20), and (35) of Heijmen, Moszynski, Wormer, and van der Avoird (1996)]

$$\begin{aligned}
&\alpha^{(1,l_{\mathrm{A}};\lambda_{\mathrm{A}},\sigma'_{\mathrm{A}})}_{\mathrm{m,A}}(Q_{r_{\mathrm{A}}}) = 2(-1)^{1-l_{\mathrm{A}}+\sigma'_{\mathrm{A}}}\sqrt{2\lambda_{\mathrm{A}}+1} \\
&\times \sum_{\sigma_1,\sigma_2}\sum_{i\neq 0} \frac{\left\langle 0 \left| Q^{(1,\sigma_1)}_{\mathrm{m,A}} \right| i \right\rangle \left\langle i \left| Q^{(l_{\mathrm{A}},\sigma_2)}_{\mathrm{m,A}} \right| 0 \right\rangle}{E_i - E_0} \begin{pmatrix} 1 & l_{\mathrm{A}} & \lambda_{\mathrm{A}} \\ \sigma_1 & \sigma_2 & -\sigma'_{\mathrm{A}} \end{pmatrix}.
\end{aligned} \tag{16-22}$$

In Eq. (16-22), $Q^{(1,\sigma_1)}_{\mathrm{m,A}}$ is component σ_1 of the irreducible spherical tensor operator representing the dipole moment. This operator depends on the nuclear and electronic coordinates; it is not averaged over the electronic wavefunction. The operator $Q^{(l_{\mathrm{A}},\sigma_2)}_{\mathrm{m,A}}$ represents the component σ_2 of the $2^{l_{\mathrm{A}}}$-pole moment, it also depends on the nuclear and electronic coordinates. The ket $|0\rangle$ represents the electronic wavefunction for the electronic state occupied by moiety A; the electronic energy of this state is E_0. All the other electronic states of the moiety are represented by kets $|i\rangle$ with corresponding energies E_i. In the matrix elements of Eq. (16-22), integration is over the electronic coordinates only. For $l_{\mathrm{A}} = 1$, we have $\lambda_{\mathrm{A}} = 0$, 1, or 2, and $\alpha^{(1,1;\lambda_{\mathrm{A}},\sigma'_{\mathrm{A}})}_{\mathrm{m,A}}(Q_{r_{\mathrm{A}}}) = \alpha^{(\lambda_{\mathrm{A}},\sigma'_{\mathrm{A}})}_{\mathrm{m}}$, where the latter quantity is a molecule fixed component of the static electric polarizability tensor, expressed in irreducible spherical tensor form [see Section 14.3]. We obtain $\alpha^{(\lambda_{\mathrm{A}},\sigma'_{\mathrm{A}})}_{\mathrm{m}}$ by replacing Q by α, s by m, and (ξ, η, ζ) by (x, y, z) in Eqs. (14-112)-(14-114).

The dipole moment induced on moiety B by the multipole moments of moiety A is obtained by interchanging A and B in Eq. (16-20) and multiplying the resulting expression by $(-1)^{\lambda_{\mathrm{B}}+\lambda_{\mathrm{AB}}-l_{\mathrm{B}}}$ [see van der Avoird, Wormer and Moszynski (1994)]. This factor is obtained in a somewhat involved derivation, in which the most important consideration is that renaming A to B and B to A causes the direction of the body fixed z axis to be reversed since this axis is defined as pointing from the center of mass of A to the center of mass of B.

In most of the methods used for calculating the rotation-vibration energies of a weakly bound cluster molecule, the molecular wavefunction is expressed as a linear combination of known basis functions. The form of the basis functions depends on the coordinates chosen to describe the molecule. For a dimer AB in the space fixed reference frame, we use the rotation-vibration Hamiltonian given in Eqs. (16-1)-(16-6). The eigenfunctions of this Hamiltonian are normally expressed in terms of the basis functions

$$\begin{aligned}
&|n, j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, l; J, m\rangle_{(\mathrm{s})} \\
&= (-1)^{j_{\mathrm{A}}-j_{\mathrm{B}}+j_{\mathrm{AB}}-l+m} \sqrt{2j_{\mathrm{AB}}+1}\sqrt{2J+1}\,\Phi_n(R, Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}}) \\
&\times \sum_{m_{\mathrm{A}},m_{\mathrm{B}}} \sum_{m_{\mathrm{AB}},m_l} (-1)^{m_{\mathrm{AB}}} \begin{pmatrix} j_{\mathrm{A}} & j_{\mathrm{B}} & j_{\mathrm{AB}} \\ m_{\mathrm{A}} & m_{\mathrm{B}} & -m_{\mathrm{AB}} \end{pmatrix} \begin{pmatrix} j_{\mathrm{AB}} & l & J \\ m_{\mathrm{AB}} & m_l & -m \end{pmatrix} \\
&\times |j_{\mathrm{A}}, k_{\mathrm{A}}, m_{\mathrm{A}}\rangle_{(\mathrm{s})} |j_{\mathrm{B}}, k_{\mathrm{B}}, m_{\mathrm{B}}\rangle_{(\mathrm{s})} Y_{lm_l}(\theta, \phi).
\end{aligned} \tag{16-23}$$

The '(s)' subscript on the symmetric top wavefunctions $|j_{\mathrm{A}}, k_{\mathrm{A}}, m_{\mathrm{A}}\rangle_{(\mathrm{s})}$ and $|j_{\mathrm{B}}, k_{\mathrm{B}}, m_{\mathrm{B}}\rangle_{(\mathrm{s})}$ indicates that these functions depend on the Euler angles (θ_{A}, ϕ_{A}, χ_{A}) and ($\theta_{\mathrm{B}}, \phi_{\mathrm{B}}, \chi_{\mathrm{B}}$), respectively. In Eq. (16-23) we can choose the function $\Phi_n(R,Q_{r_{\mathrm{A}}},Q_{r_{\mathrm{B}}})$ as a product of harmonic oscillator functions describing the vibrational motion of the moieties, multiplied by basis functions describing the intermolecular stretching motion. These latter functions can for example be chosen as the Morse oscillator eigenfunctions or the distributed Gaussian functions mentioned in Section 13.2.5. The basis function in Eq. (16-23) is an eigenfunction of $\hat{\jmath}_{\mathrm{A}}{}^2$ (with associated quantum number j_{A}), $\hat{\jmath}_{\mathrm{B}}{}^2$ (with associated quantum number j_{B}), of the internal angular momentum $\hat{\jmath}_{\mathrm{AB}}{}^2$ (with associated quantum number j_{AB}), and of the end-over-end angular momentum $\hat{l}^2$ (with associated quantum number l). Further, it is an eigenfunction of the rovibronic angular momentum operator $\hat{\boldsymbol{J}}^2$ and the space fixed component $\hat{J}_\zeta$ with associated quantum numbers J and m, respectively; we obtain such an eigenfunction by using Eq. (10-98) twice. When we calculate the matrix elements of the intermolecular potential energy given by Eq. (16-6) between the basis functions in Eq. (16-23), we obtain the integrals over the Euler angles in analytical form from Eqs. (11-13), (11-19), and (14-23) in conjunction with the Wigner-Eckart theorem [Eq. (14-24)].

If a body fixed axis system is used to define the Hamiltonian, we employ the following basis functions

$$
\begin{aligned}
&|n, j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, k; J, m\rangle_{(\mathrm{m})} \\
&= (-1)^{j_{\mathrm{A}}-j_{\mathrm{B}}+k}\sqrt{2j_{\mathrm{AB}}+1}\,\Phi_n(R, Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}}) \\
&\times \sum_{m_{\mathrm{A}}, m_{\mathrm{B}}} \begin{pmatrix} j_{\mathrm{A}} & j_{\mathrm{B}} & j_{\mathrm{AB}} \\ m_{\mathrm{A}} & m_{\mathrm{B}} & -k \end{pmatrix} \\
&\times |j_{\mathrm{A}}, k_{\mathrm{A}}, m_{\mathrm{A}}\rangle_{(\mathrm{m})}\,|j_{\mathrm{B}}, k_{\mathrm{B}}, m_{\mathrm{B}}\rangle_{(\mathrm{m})}\,S_{Jkm}(\theta, \phi),
\end{aligned}
\tag{16-24}
$$

where the function $S_{Jkm}(\theta, \phi)$ is defined in Eqs. (11-15) and (11-16). The symmetric top wavefunctions $|j_{\mathrm{A}}, k_{\mathrm{A}}, m_{\mathrm{A}}\rangle_{(\mathrm{m})}$ and $|j_{\mathrm{B}}, k_{\mathrm{B}}, m_{\mathrm{B}}\rangle_{(\mathrm{m})}$ depend on the Euler angles $(\theta_{\mathrm{A}}^{\mathrm{m}}, \phi_{\mathrm{A}}^{\mathrm{m}}, \chi_{\mathrm{A}}^{\mathrm{m}})$ and $(\theta_{\mathrm{B}}^{\mathrm{m}}, \phi_{\mathrm{B}}^{\mathrm{m}}, \chi_{\mathrm{B}}^{\mathrm{m}})$, respectively. The basis function in Eq. (16-24) is a simultaneous eigenfunction of $\hat{j}_{\mathrm{A}}{}^2$ (with associated quantum number j_{A}), $\hat{j}_{\mathrm{B}}{}^2$ (with associated quantum number j_{B}), and of $\hat{j}_{\mathrm{AB}}{}^2$ (with associated quantum number j_{AB}). Further, it is an eigenfunction of $\hat{\boldsymbol{J}}^2$, the body fixed component $\hat{J}_z$, and the space fixed component $\hat{J}_\zeta$ with associated quantum numbers J, k, and m, respectively. The Euler angles $\phi_{\mathrm{A}}^{\mathrm{m}}$ and $\phi_{\mathrm{B}}^{\mathrm{m}}$ describe the rotation around the body fixed z axis of the two moieties, and $\phi_{\mathrm{B}}^{\mathrm{m}} - \phi_{\mathrm{A}}^{\mathrm{m}}$ is the torsional angle. If we extract from Eq. (16-24) the factor $S_{Jkm}(\theta, \phi)$ describing the end-over-end rotation and the factors depending on $\phi_{\mathrm{A}}^{\mathrm{m}}$ and $\phi_{\mathrm{B}}^{\mathrm{m}}$, we obtain the zero order rotational-torsional basis function

$$
\Phi_{\mathrm{rt}} = [(1/(2\pi)]S_{Jkm}(\theta, \phi)\exp(im_{\mathrm{A}}\phi_{\mathrm{A}}^{\mathrm{m}})\exp(im_{\mathrm{B}}\phi_{\mathrm{B}}^{\mathrm{m}}),
\tag{16-25}
$$

where the two complex exponential factors come from the symmetric top wavefunctions $|j_{\mathrm{A}}, k_{\mathrm{A}}, m_{\mathrm{A}}\rangle_{(\mathrm{m})}$ and $|j_{\mathrm{B}}, k_{\mathrm{B}}, m_{\mathrm{B}}\rangle_{(\mathrm{m})}$, respectively [see Eq. (11-15)]. The nonvanishing terms in Eq. (16-24) have $k = m_{\mathrm{A}} + m_{\mathrm{B}}$. If this condition is not fulfilled the $3j$-symbol vanishes. We see that the rotational-torsional basis functions Φ_{rt} used for a dimer described in a body fixed axis system are identical to those given for dimethylacetylene in Eq. (15-84). The angles $\phi_{\mathrm{A}}^{\mathrm{m}}$ and $\phi_{\mathrm{B}}^{\mathrm{m}}$ used for the dimer are analogous in definition to the angles χ_a and χ_b in Eq. (15-84). The relationship between the basis functions in Eqs. (16-23) and (16-24) is discussed in detail by van der Avoird, Wormer, and Moszynski (1994).

For later use in obtaining optical selection rules, we derive here the matrix elements of the 'space fixed' dipole moment component $\mu_{\mathrm{s}}^{(1,\sigma)}$ in Eq. (16-13) between the basis functions in Eq. (16-23). These matrix elements are fairly straightforwardly obtained from the standard results of angular momentum theory. The derivation involves repeated use of the Wigner-Eckart theorem [Eq. (14-24)], of Eq. (5.68) of Zare (1988), and of the fact that the rotation matrix elements $D_{\sigma\sigma''}^{(\omega)*}$, $\sigma = -\omega, -\omega+1, \ldots, \omega$, are irreducible spherical tensor operators of rank ω. The reduced matrix element associated with these operators can be obtained from Eq. (14-25) by setting $U_{\mathrm{m}}^{(\omega,\sigma')} = \delta_{\sigma'\sigma''}$ [see also Eq. (25) of Bowater, Brown, and Carrington (1973)]. We obtain the matrix element

$$
\left\langle n', j_{\mathrm{A}}', k_{\mathrm{A}}', j_{\mathrm{B}}', k_{\mathrm{B}}', j_{\mathrm{AB}}', l'; J', m' \left| \mu_{\mathrm{s}}^{(1,\sigma)} \right| n'', j_{\mathrm{A}}'', k_{\mathrm{A}}'', j_{\mathrm{B}}'', k_{\mathrm{B}}'', j_{\mathrm{AB}}'', l''; J'', m'' \right\rangle_{(\mathrm{s})}
$$

$$
\begin{aligned}
&= (-1)^{J''-m'+j''_{\mathrm{A}}+k'_{\mathrm{A}}+j''_{\mathrm{B}}+k'_{\mathrm{B}}+l''+1}\sqrt{3(2J'+1)(2J''+1)(2j'_{\mathrm{AB}}+1)(2j''_{\mathrm{AB}}+1)} \\
&\times \sqrt{(2j'_{\mathrm{A}}+1)(2j''_{\mathrm{A}}+1)(2j'_{\mathrm{B}}+1)(2j''_{\mathrm{B}}+1)(2l'+1)(2l''+1)} \\
&\times \begin{pmatrix} J'' & 1 & J' \\ m'' & \sigma & -m' \end{pmatrix} \sum_{\Lambda,\lambda_{\mathrm{R}}} (-1)^{\lambda_{\mathrm{A}}+\lambda_{\mathrm{B}}+\lambda_{\mathrm{R}}}\sqrt{2\lambda_{\mathrm{AB}}+1} \\
&\times \left\langle \Phi_{n'} \left| \mu^{(\mathrm{s})}_{\Lambda,\lambda_{\mathrm{R}}} \right| \Phi_{n''} \right\rangle \begin{Bmatrix} j'_{\mathrm{AB}} & j''_{\mathrm{AB}} & \lambda_{\mathrm{AB}} \\ l' & l'' & \lambda_{\mathrm{R}} \\ J' & J'' & 1 \end{Bmatrix} \begin{Bmatrix} j'_{\mathrm{A}} & j''_{\mathrm{A}} & \lambda_{\mathrm{A}} \\ j'_{\mathrm{B}} & j''_{\mathrm{B}} & \lambda_{\mathrm{B}} \\ j'_{\mathrm{AB}} & j''_{\mathrm{AB}} & \lambda_{\mathrm{AB}} \end{Bmatrix} \\
&\times \begin{pmatrix} j''_{\mathrm{A}} & \lambda_{\mathrm{A}} & j'_{\mathrm{A}} \\ k''_{\mathrm{A}} & \sigma'_{\mathrm{A}} & -k'_{\mathrm{A}} \end{pmatrix} \begin{pmatrix} j''_{\mathrm{B}} & \lambda_{\mathrm{B}} & j'_{\mathrm{B}} \\ k''_{\mathrm{B}} & \sigma'_{\mathrm{B}} & -k'_{\mathrm{B}} \end{pmatrix} \begin{pmatrix} l'' & \lambda_{\mathrm{R}} & l' \\ 0 & 0 & 0 \end{pmatrix}. \qquad (16\text{-}26)
\end{aligned}
$$

where $\Lambda = \lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{A}}\sigma'_{\mathrm{B}}$ and the quantities in braces are $9j$-symbols [see, for example, Zare (1988)]. Inserting the matrix element of Eq. (16-26) into Eq. (14-17) gives the line strength of a rotation-vibration transition. The first $3j$-symbol in Eq. (16-26) gives the usual selection rule $\Delta J = 0, \pm 1$. The summations over σ, m', and m'' entering into the expression for the line strength will involve the square of this $3j$-symbol; these summations are carried out by means of Eq. (14-32). For a $3j$-symbol to be nonvanishing, a triangular condition $\Delta(j_1 j_2 j_3)$[1] must be satisfied by the numbers $j_1 j_2 j_3$ in its upper row. In order for a $9j$-symbol not to vanish, six triangular conditions must be satisfied, one for each row and one for each column.

For a dimer described in the body fixed reference frame, we require the matrix elements of $\mu_{\mathrm{s}}^{(1,\sigma)}$ between the basis functions in Eq. (16-24) for calculating the line strength. The operator $\mu_{\mathrm{s}}^{(1,\sigma)}$ is expressed by Eq. (16-15), where the body fixed component $\mu_{\mathrm{m}}^{(1,\sigma')}$ is given by Eq. (16-16). The basis function in Eq. (16-24) is obtained as a 'vibrational' basis function multiplied by the rotational basis function $S_{Jkm}(\theta, \phi)$, and the first step towards obtaining the line strength is to derive the matrix elements of $\mu_{\mathrm{m}}^{(1,\sigma')}$ between the vibrational basis functions. These matrix elements can, in principle, be obtained from standard angular momentum theory. However, we have the added complexity that we are coupling angular momentum eigenfunctions and irreducible spherical tensor operators labeled by quantum numbers $m_{\mathrm{A}}, m_{\mathrm{B}}, \ldots$, measuring projections of the angular momentum along body fixed axes. The results of standard angular momentum theory as given, for example, in Zare (1988) are derived under the assumption that all angular momentum components satisfy the commutation relations of Eq. (10-90). The body fixed components (J_x, J_y, J_z) of the angular momentum obey the commutation relations of Eq. (10-92), and the three reversed components [see Van Vleck (1951)] $(-J_x, -J_y, -J_z)$ satisfy the commutation relations of Eq. (10-90), so we can apply the Wigner-Eckart theorem and all the related results to the body fixed angular momentum components, and the eigenfunctions and irreducible spherical tensor operators associated with them, by reversing the signs of all quantum numbers describing projections on body fixed axes. In this manner we can derive an expression for the matrix elements of $\mu_{\mathrm{m}}^{(1,\sigma')}$ between the vibrational basis functions. With these matrix elements we can obtain the matrix elements of $\mu_{\mathrm{s}}^{(1,\sigma)}$ between the basis functions in Eq. (16-24) from Eq. (16-15). We must derive the rotational matrix element $\left\langle S_{J'k'm'} \left| [D_{\sigma\sigma'}^{(1)}(\phi,\theta,0)]^* \right| S_{J''k''m''} \right\rangle$ which involves integration over the Euler angles θ and ϕ only. It turns out that the matrix elements of $\mu_{\mathrm{m}}^{(1,\sigma')}$ between the vibrational basis vanish unless $\sigma' = k' - k''$. With this restriction, it is easy to show that the rotational matrix element of $[D_{\sigma\sigma'}^{(1)}(\phi,\theta,0)]^*$ is given by the right hand side of Eq. (14-23) [in which we replace N by J]. These considerations lead to:

---

[1] Where $\Delta(j_1 j_2 j_3)$ indicates that $|j_2 - j_3| \leq j_1 \leq j_2 + j_3$ and $|j_1 - j_3| \leq j_2 \leq j_1 + j_3$ and $|j_1 - j_2| \leq j_3 \leq j_1 + j_2$. These conditions ensure that j_1, j_2, and j_3 could be the lengths of the sides in a triangle.

$$
\begin{aligned}
&\left\langle n', j'_{\mathrm{A}}, k'_{\mathrm{A}}, j'_{\mathrm{B}}, k'_{\mathrm{B}}, j'_{\mathrm{AB}}, k'; J', m' \left| \mu_{\mathrm{s}}^{(1,\sigma)} \right| n'', j''_{\mathrm{A}}, k''_{\mathrm{A}}, j''_{\mathrm{B}}, k''_{\mathrm{B}}, j''_{\mathrm{AB}}, k''; J'', m'' \right\rangle_{(\mathrm{m})} \\
&= (-1)^{j'_{\mathrm{A}}+j'_{\mathrm{B}}+j'_{\mathrm{AB}}+k'_{\mathrm{A}}+k'_{\mathrm{B}}+m'} \sqrt{(2J'+1)(2J''+1)(2j'_{\mathrm{AB}}+1)(2j''_{\mathrm{AB}}+1)} \\
&\times \sqrt{(2j'_{\mathrm{A}}+1)(2j''_{\mathrm{A}}+1)(2j'_{\mathrm{B}}+1)(2j''_{\mathrm{B}}+1)} \\
&\times \begin{pmatrix} J'' & 1 & J' \\ m'' & \sigma & -m' \end{pmatrix} \sum_{\Lambda,\sigma'} \sqrt{2\lambda_{\mathrm{AB}}+1} \\
&\times \left\langle \Phi_{n'} \left| \mu_{\Lambda,\sigma'}^{(\mathrm{m})} \right| \Phi_{n''} \right\rangle \begin{pmatrix} J'' & 1 & J' \\ k'' & \sigma' & -k' \end{pmatrix} \begin{Bmatrix} j'_{\mathrm{A}} & j''_{\mathrm{A}} & \lambda_{\mathrm{A}} \\ j'_{\mathrm{B}} & j''_{\mathrm{B}} & \lambda_{\mathrm{B}} \\ j'_{\mathrm{AB}} & j''_{\mathrm{AB}} & \lambda_{\mathrm{AB}} \end{Bmatrix} \\
&\times \begin{pmatrix} j''_{\mathrm{A}} & \lambda_{\mathrm{A}} & j'_{\mathrm{A}} \\ k''_{\mathrm{A}} & \sigma'_{\mathrm{A}} & -k'_{\mathrm{A}} \end{pmatrix} \begin{pmatrix} j''_{\mathrm{B}} & \lambda_{\mathrm{B}} & j'_{\mathrm{B}} \\ k''_{\mathrm{B}} & \sigma'_{\mathrm{B}} & -k'_{\mathrm{B}} \end{pmatrix} \begin{pmatrix} j''_{\mathrm{AB}} & \lambda_{\mathrm{AB}} & j'_{\mathrm{AB}} \\ k'' & \sigma' & -k' \end{pmatrix} \qquad (16\text{-}27)
\end{aligned}
$$

where, again, the first $3j$-symbol gives $\Delta J = 0, \pm 1$. As usual, in obtaining the line strength this $3j$-symbol is "summed away" by means of Eq. (14-32).

16.4 SOLVING THE SCHRÖDINGER EQUATION

There are six general ways that are regularly used in the literature for solving the Schrödinger equation for weakly bound cluster molecules. These are the variational method, the discrete variable representation (DVR) technique, the collocation method, the close-coupling method, the variational Monte Carlo method, and the diffusion quantum Monte Carlo method.

In a variational calculation, the rotation-vibration wavefunctions are expressed in a Finite Basis Representation [FBR, see Section 13.2.5] of basis functions such as those given in Eqs. (16-23) and (16-24), the corresponding matrix representation of the rotation-vibration Hamiltonian is constructed and diagonalized numerically.

The DVR technique starts by expressing the wavefunctions in an FBR but transforms the resulting coupled equations to an equivalent set of coupled equations, labeled by discrete values of some of the coordinates. This method has been discussed briefly in Section 13.2.5.

F 1

The collocation method [Peet and Yang (1989a, 1989b); Yang, Peet, and Miller (1989)] is closely related to the DVR method. The wavefunctions are given in an FBR, and a set of coupled equations in the expansion coefficients is obtained by requiring that the Schrödinger equation be exactly satisfied at a finite number of discrete coordinate values.

If we are using a space fixed reference frame Hamiltonian in a close-coupling calculation, we write the wavefunction as

$$\Phi_{\mathrm{rv}} = \sum_{\Lambda, n^{(Q)}} \Phi_{n^{(R)};\Lambda,n^{(Q)}}(R) \left| n^{(Q)}, j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, l; J, m \right\rangle_{(\mathrm{s})}, \tag{16-28}$$

where the compound index $\Lambda = j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, l$ and

$$\begin{aligned} &\left| n^{(Q)}, j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, l; J, m \right\rangle_{(\mathrm{s})} \\ &= (-1)^{j_{\mathrm{A}}-j_{\mathrm{B}}+j_{\mathrm{AB}}-l+m} \sqrt{2j_{\mathrm{AB}}+1}\sqrt{2J+1}\, \Phi_{n^{(Q)}}(Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}}) \\ &\times \sum_{m_{\mathrm{A}},m_{\mathrm{B}}} \sum_{m_{\mathrm{AB}},m_l} (-1)^{m_{\mathrm{AB}}} \begin{pmatrix} j_{\mathrm{A}} & j_{\mathrm{B}} & j_{\mathrm{AB}} \\ m_{\mathrm{A}} & m_{\mathrm{B}} & -m_{\mathrm{AB}} \end{pmatrix} \begin{pmatrix} j_{\mathrm{AB}} & l & J \\ m_{\mathrm{AB}} & m_l & -m \end{pmatrix} \\ &\times |j_{\mathrm{A}}, k_{\mathrm{A}}, m_{\mathrm{A}}\rangle_{(\mathrm{s})} |j_{\mathrm{B}}, k_{\mathrm{B}}, m_{\mathrm{B}}\rangle_{(\mathrm{s})} Y_{lm_l}(\theta,\phi). \end{aligned} \tag{16-29}$$

In Eq. (16-29), $\Phi_{n^{(Q)}}(Q_{r_{\mathrm{A}}}, Q_{r_{\mathrm{B}}})$ is a known basis function, chosen for example as a product of harmonic oscillator functions depending on the normal coordinates of the two moieties. We insert the wavefunction of Eq. (16-28) in the Schrödinger equation for the rotation and vibration, multiply the left and right hand sides of the resulting equation by one of the functions $|n^{(Q)}, j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, l; J, m\rangle_{(\mathrm{s})}$, and integrate the two products over all coordinates except R. We obtain a set of coupled equations (one for each of the basis functions $|n^{(Q)}, j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, l; J, m\rangle_{(\mathrm{s})}$) in the unknown R-dependent functions $\Phi_{n^{(R)};\Lambda,n^{(Q)}}(R)$. These equations are solved by means of numerical propagator methods developed for scattering problems [see, for example, Johnson (1973)]; such calculations produce the values of the radial wavefunctions $\Phi_{n^{(R)};\Lambda,n^{(Q)}}(R)$ on a grid of equidistantly spaced R values. One iterates to find the energies for which the corresponding radial wavefunctions $\Phi_{n^{(R)};\Lambda,n^{(Q)}}(R) \to 0$ for $R \to 0$ and remain finite at $R = 0$.

In the variational Monte Carlo method [Rick, Lynch, and Doll (1991), Bačić, Kennedy-Mandziuk, Moskowitz, and Schmidt (1992)], a parameterized analytical form of the wavefunction (i.e., a *trial* wavefunction $\Phi_{\mathrm{rv}}^{(\mathrm{trial})}$) is chosen. The parameter values producing the optimum wavefunction are determining by minimizing the functional

$$E = \frac{\left\langle \Phi_{\mathrm{rv}}^{(\mathrm{trial})} \middle| \hat{H}_{\mathrm{rv}} \middle| \Phi_{\mathrm{rv}}^{(\mathrm{trial})} \right\rangle}{\left\langle \Phi_{\mathrm{rv}}^{(\mathrm{trial})} | \Phi_{\mathrm{rv}}^{(\mathrm{trial})} \right\rangle}. \tag{16-30}$$

The expectation value in the numerator is calculated by means of a random-walk algorithm, this is the Monte Carlo aspect of such a calculations. By choosing the trial wavefunction to have a particular symmetry in the MS group the lowest energy associated with a state of this symmetry can be calculated for $J = 0$. Monte Carlo methods for calculating excited states of any given MS group symmetry, or states having nonzero J value, have not yet been developed. Clearly this limits the usefulness of the method. However, weakly bound cluster molecules are often studied in molecular jets at very low temperatures, and only a few low-lying states are populated. Thus the energies obtained from the variational Monte Carlo calculation can be sufficient to enable one to understand the experimental data.

Diffusion Monte Carlo calculations [see Anderson (1975), Coker and Watts (1986), and Buch (1992)] are based on the time-dependent Schrödinger equation

$$-i\hbar\frac{\partial\Psi}{\partial t} = -H\Psi = -T\Psi - V\Psi \tag{16-31}$$

which describes the development in time of a wavefunction Ψ. By substituting $\tau = it/\hbar$ in Eq. (16-31) and by inserting the expression for the kinetic energy operator *in Cartesian coordinates* [i.e., in solving the rotation-vibration Schrödinger equation we would use the nuclear kinetic energy operator in Eq. (10-2) which is expressed in terms of the (ξ_i, η_i, ζ_i) coordinates, and we would have to neglect the second term involving $\nabla_i \cdot \nabla_j$] we obtain an equation which is formally identical to a differential equation encountered in the theoretical description of diffusion. It is well known that this latter equation can be solved by means of a random-walk algorithm, and the same algorithm can be used to solve the quantum mechanical problem. Again only the lowest state of each symmetry, and only $J = 0$ states, can be calculated. But, as mentioned above, this still enables some important understanding to be achieved. Obviously, the diffusion Monte Carlo method is an example of a direct method for solving the molecular Schrödinger equation [see the discussion at the beginning of Chapter 9]. Diffusion Monte Carlo calculations can be carried out for large clusters. For example, the method has been applied to calculate the zero-point averaged structure of the water hexamer using a model theoretical intermoiety potential, and this gives good agreement with the experimentally determined ground state rotational constants A_0, B_0 and C_0 [Liu, Brown, Carter, Saykally, Gregory, and Clary (1996)].

Various more approximate techniques are also used in which there is an adiabatic separation of some of the contortional coordinates, or perhaps even the complete neglect of some of them [see, for example, Althorpe, Clary and Bunker (1991)]. The review paper by van der Avoird, Wormer and Moszynski (1994) discusses the methods used, and many references to the literature are given.

16.5 EXAMPLES

We discuss two examples. The first, the hydrogen dimer, is an example in which the intermolecular potential is only weakly anisotropic. In this case the space fixed reference frame Hamiltonian is appropriate. The second example, the ammonia dimer, is much more complicated but it provides a very good example of a cluster with a body fixed reference frame Hamiltonian. We also use it to explain the problems encountered when using a large MS group; for the ammonia dimer an MS group of order 144 is required. By working through these two examples the reader will learn general techniques that are important for understanding the symmetry properties, and the use of such properties, for weakly bound cluster molecules.

16.5.1 The hydrogen dimer

As an example using space fixed coordinates we consider the symmetry classification of the rotation-contortion-vibration states of the hydrogen dimer, and the symmetry restrictions on electric dipole transitions. For more details concerning the spectrum of the hydrogen dimer, and of the theory needed to interpret it, see Bunker (1979b), McKellar (1990), Schaefer (1994), and the references therein. We consider the following isotopomers: $(H_2)_2$, $(D_2)_2$, $(HD)_2$, H_2-D_2, and H_2-HD. The general symmetry results quoted for $(H_2)_2$ and $(D_2)_2$ are applicable to weakly anisotropic dimers such as $(N_2)_2$ and $(O_2)_2$, and the results for $(HD)_2$ and H_2-HD are applicable to $(CO)_2$ and N_2-CO respectively. A theoretical calculation of the infrared spectrum $(N_2)_2$ has been published by Brocks and van der Avoird (1985), and $(CO)_2$ has been considered by van der Pol, van der Avoird and Wormer (1990), Bunker, Jensen, Althorpe and Clary (1993), and Meredith and Stone (1998).

The MS group for $(H_2)_2$ or $(D_2)_2$ is the group $\boldsymbol{G}_{16}$ given[2] in Table A-25; we use the MW convention for labeling the irreducible representations. The convention used for labeling the nuclei, and the definition of the nine space fixed coordinates $(r_A,\theta_A,\phi_A,r_B,\theta_B,\phi_B,R,\theta,\phi)$, are given in Fig 16-1. The rotation-contortion-vibration wavefunctions and the dipole moment function will involve these coordinates, and the transformation properties of the coordinates in $\boldsymbol{G}_{16}$ are given in Table 16-1.

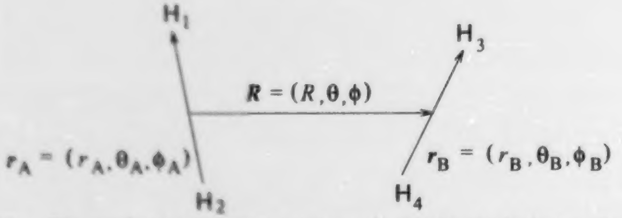
H_1
H_3
$\boldsymbol{R} = (R,\theta,\phi)$
$\boldsymbol{r}_A = (r_A,\theta_A,\phi_A)$
$\boldsymbol{r}_B = (r_B,\theta_B,\phi_B)$
H_2
H_4

Fig. 16-1. The numbering convention and coordinates for the hydrogen dimer.

The rotation-vibration wavefunction of a single hydrogen molecule in the state (v,j) is $\Phi_v(r)Y_{jm}(\theta,\phi)$, and basis functions for the rotation-contortion-

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[2] Omitting the permutation (56).

Table 16-1

The transformation properties of the coordinates in G_{16}.

E	$(1423)^*$	$(12)(34)$	$(13)(24)$	$(34)^*$	E^*
θ_A	$\pi-\theta_B$	$\pi-\theta_A$	θ_B	$\pi-\theta_A$	$\pi-\theta_A$
ϕ_A	$\phi_B+\pi$	$\phi_A+\pi$	ϕ_B	$\phi_A+\pi$	$\phi_A+\pi$
r_A	r_B	r_A	r_B	r_A	r_A
θ_B	θ_A	$\pi-\theta_B$	θ_A	θ_B	$\pi-\theta_B$
ϕ_B	ϕ_A	$\phi_B+\pi$	ϕ_A	ϕ_B	$\phi_B+\pi$
r_B	r_A	r_B	r_A	r_B	r_B
θ	θ	θ	$\pi-\theta$	$\pi-\theta$	$\pi-\theta$
ϕ	ϕ	ϕ	$\phi+\pi$	$\phi+\pi$	$\phi+\pi$
R	R	R	R	R	R

vibration states of $(H_2)_2$ and $(D_2)_2$ are:

$$\Phi_{\mathrm{rcv}} = |v_A v_B \pm\rangle |j_A j_B \pm\rangle |n\rangle |l\rangle, \tag{16-32}$$

where

$$|v_A v_B \pm\rangle = \Phi_{vA}(r_A)\Phi_{vB}(r_B) \pm \Phi_{vA}(r_B)\Phi_{vB}(r_A), \tag{16-33}$$

$$|j_A j_B \pm\rangle = Y_{j_A m_A}(\theta_A \phi_A) Y_{j_B m_B}(\theta_B \phi_B) \pm Y_{j_A m_A}(\theta_B \phi_B) Y_{j_B m_B}(\theta_A \phi_A) \tag{16-34}$$

and

$$|l\rangle = Y_{lm}(\theta, \phi). \tag{16-35}$$

We have introduced the vibrational quantum numbers v_A and v_B for the hydrogen moieties, and n for the intermoiety bond, and the similar rotational quantum numbers j_A, j_B and l (with space fixed component quantum numbers m_A, m_B and m_l). The two angular momenta $\mathbf{j}_A$ and $\mathbf{j}_B$ are coupled to give $\mathbf{j}_{AB}$, and $\mathbf{j}_{AB}$ and $\mathbf{l}$ are coupled to give $\mathbf{J}$, the total angular momentum. A given (j_A, j_B, l) state gives rise to many different J levels [$J = j_A + j_B + l$, $j_A + j_B + l - 1$, $\ldots$, $||\, j_A - j_B \,| - l|$; see Eq. (7-45)], and these are split apart by anisotropic terms in the potential function [see Fig. 17 of McKellar (1990)]. To determine the symmetries of the angular basis wavefunctions in G_{16} from the results in Table 16-1 we use the result[3] that

$$Y_{Jm}(\pi - \theta, \phi + \pi) = (-1)^J Y_{Jm}(\theta, \phi). \tag{16-36}$$

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[3] This can be seen by using Eq. (11-19) to relate $Y_{Jm}(\theta, \phi)$ to the symmetric top function $|J0m\rangle$, and then using Eq. (12-47) with $k = 0$ to determine the transformation property.

The symmetries of the basis functions are given in Table 16-2. The coupled wavefunctions $|j_{\mathrm{AB}}, m_{\mathrm{AB}}\rangle$ are written in terms of the uncoupled wavefunctions $|j_{\mathrm{A}}, m_{\mathrm{A}}\rangle|j_{\mathrm{B}}, m_{\mathrm{B}}\rangle$, and hence in terms of the MS group symmetry adapted combinations $|j_{\mathrm{A}} j_{\mathrm{B}} \pm\rangle$, using Eq. (10-98) with $N = j_{\mathrm{A}}$, $S = j_{\mathrm{B}}$ and $J = j_{\mathrm{AB}}$. When $j_{\mathrm{A}} = j_{\mathrm{B}}$ the relation

$$\begin{pmatrix} j_{\mathrm{A}} & j_{\mathrm{A}} & j_{\mathrm{AB}} \\ m_{\mathrm{A}} & m_{\mathrm{B}} & -m_{\mathrm{AB}} \end{pmatrix} = (-1)^{j_{\mathrm{AB}}} \begin{pmatrix} j_{\mathrm{A}} & j_{\mathrm{A}} & j_{\mathrm{AB}} \\ m_{\mathrm{B}} & m_{\mathrm{A}} & -m_{\mathrm{AB}} \end{pmatrix} \tag{16-37}$$

is used in Eq. (10-98) to determine the effect of the evenness or oddness of j_{AB} on whether the + or − combinations of uncoupled wavefunctions are present in the coupled wavefunction (see footnote to Table 16-2).

Table 16-2

The symmetries of the basis wavefunctions of $(\mathrm{H}_2)_2$ and $(\mathrm{D}_2)_2$ in G_{16}.

Function	Symmetry	
$\lvert v_{\mathrm{A}} v_{\mathrm{B}} +\rangle$	A_1^+	
$\lvert v_{\mathrm{A}} v_{\mathrm{B}} -\rangle$	B_2^+	
$\lvert j_{\mathrm{A}} j_{\mathrm{B}} +\rangle^a$	A_1^+ (j_{A} and j_{B} even), B_1^+ (j_{A} and j_{B} odd)	E^- (one odd one even)
$\lvert j_{\mathrm{A}} j_{\mathrm{B}} -\rangle^a$	B_2^+ (j_{A} and j_{B} even), A_2^+ (j_{A} and j_{B} odd)	
$\lvert l\rangle$	A_1^+ (l even), A_2^- (l odd)	
$\lvert n\rangle$	A_1^+	

[a] If $j_{\mathrm{A}} = j_{\mathrm{B}}$ coupled functions having j_{AB} even can only contain $|j_{\mathrm{A}} j_{\mathrm{A}} +\rangle$ functions, and coupled functions having j_{AB} odd can only contain $|j_{\mathrm{A}} j_{\mathrm{A}} -\rangle$ functions [see Eq. (16-37)].

Applying the statistical formulae we find that the overall wavefunctions can only be of symmetry B_1^+ or A_1^- for $(\mathrm{H}_2)_2$, and of symmetry A_1^+ or B_1^- for $(\mathrm{D}_2)_2$. As usual this restricts the nuclear spin states that each rotation-contortion-vibration state can be combined with, and it gives rise to nuclear spin statistical weights (see Chapter 8). It is helpful to think of the nuclear spin states of the moieties in building up the nuclear spin states of the dimer. As discussed in Section 13.6.3 there are two nuclear spin states for an H_2 molecule: a *para* state having $I = 0$, and an *ortho* state having $I = 1$. In an H_2 molecule the para state can only be combined with $J =$ even rotation-vibration wavefunctions, and the ortho state with $J =$ odd wavefunctions. In the $(\mathrm{H}_2)_2$ dimer we can talk about a (para-para) form as one built up from two para moieties, and there are also (ortho,ortho) and (ortho,para) forms. By considering transformation properties in G_{16} we determine that the (para-para) form has j_{A} and j_{B} both even, $I = 0$, and nuclear spin symmetry ${}^1B_1^+$.

The (para-ortho) form has (j_A, j_B) = (even,odd) or (odd,even), $I = 1$, and nuclear spin symmetry ${}^3E^+$. The (ortho-ortho) form has j_A and j_B both odd, $I = 0$, 1 or 2 with nuclear spin symmetries ${}^1A_1{}^+$, ${}^3B_2{}^+$ or ${}^5A_1{}^+$, respectively. The nuclear spin statistical weights for $(H_2)_2$ are the same as for torsionally tunneling ethylene given in Table 8-2:

$$\Gamma^{sw}_{rve} = A_1{}^+ \oplus B_1{}^- \oplus 3(A_2{}^+ \oplus B_2{}^-) \oplus 6(A_1{}^- \oplus B_1{}^+) \oplus 3(E^+ \oplus E^-), \tag{16-38}$$

and states of symmetry $A_2{}^-$ or $B_2{}^+$ are missing. The statistical weights for $(D_2)_2$ or $({}^{14}N_2)_2$ are given by

$$\begin{aligned}\Gamma^{sw}_{rve} =& 21(A_1{}^+ \oplus B_1{}^-) \oplus 3(A_2{}^+ \oplus B_2{}^-) \oplus 6(A_1{}^- \oplus B_1{}^+)\\ &\oplus 15(A_2{}^- \oplus B_2{}^+) \oplus 18(E^+ \oplus E^-),\end{aligned} \tag{16-39}$$

and there are no missing levels, whereas for $({}^{16}O_2)_2$ the statistical weights are

$$\Gamma^{sw}_{rve} = A_1{}^+ \oplus B_1{}^- \tag{16-40}$$

and many levels are missing (because only moiety states having N even exist).

The coarse rotation-vibration energy level structure is determined by the values of the hydrogen moiety quantum numbers v_A, v_B, j_A and j_B, and the fine structure is determined by the values of the R-stretching quantum number n and the end-over-end rotational quantum number l. For $(H_2)_2$ the levels with $n \geq 1$ and $l \geq 2$ are above the dissociation energy D_0 (about 3 cm^{-1}) of the intermoiety bond, and the energy separation between the $l = 1$ and 0 states is about 1.5 cm^{-1}. There will be further splittings [typically of the order of 0.3 cm^{-1} in $(H_2)_2$] caused by the anisotropy of the potential and giving the J structure of a given (j_A, j_B, j_{AB}, l) state [see Table III of McKellar and Schaefer (1991)]. The best available interaction potential for $(H_2)_2$ is that of Schaefer (1994) which has been determined by adjusting a previously obtained *ab initio* potential [Schaefer and Meyer (1979), Schaefer and Köhler (1989)]. In the notation of Eq. (16-6) only the terms $V_\Omega(R,0,0)$ with Ω = 000, 022, 202 $(V_{022} = V_{202})$ and 224 occur, and the isotropic term (i.e., the term having Ω = 000) dominates. Nuclear spin hyperfine structure produces splittings in the 100 kHz range [Verberne and Reuss (1980,1981)].

In Table 16-3 we give the wavefunctions, j_{AB} values, symmetries (called Γ_{coarse}) and zero order wavenumbers for some of the coarse (v_A, v_B, j_A, j_B) structure in $(H_2)_2$ and $(D_2)_2$. Degeneracies such as those between the zero order states $(|\,10;00\,\rangle + |\,00;10\,\rangle)$ and $(|\,10;00\,\rangle - |\,00;10\,\rangle)$ will be resolved by coupling terms in the potential function that depend on R and on the moiety bond lengths r_A and r_B. The symmetry Γ_{rcv} of a rotation-contortion-vibration level is obtained by multiplying Γ_{coarse} by $A_1{}^+$ or $A_2{}^-$ as l is even or odd respectively. For given values of j_{AB} and l each of the possible J levels (J = $j_{AB} + l$, $j_{AB} + l - 1$, ..., $|j_{AB} - l|$) has the same symmetry Γ_{rcv}. The (n,l) structure is built on the coarse energy level structure like rotational structure

Table 16-3

Coarse energy level structure (in cm^{-1}) for $(H_2)_2$ and $(D_2)_2$.

$\lvert v_A j_A; v_B j_B\rangle$	j_{AB}	Γ_{coarse}	$(H_2)_2$	$(D_2)_2$
$\lvert 11;03\rangle - \lvert 03;11\rangle$	2,3,4	$A_2{}^+$	4979.2	3408.5
$\lvert 11;03\rangle + \lvert 03;11\rangle$	2,3,4	$B_1{}^+$		
$\lvert 13;01\rangle - \lvert 01;13\rangle$	2,3,4	$A_2{}^+$	4949.8	3398.0
$\lvert 13;01\rangle + \lvert 01;13\rangle$	2,3,4	$B_1{}^+$		
$\lvert 03;10\rangle, \lvert 10;03\rangle$	3	E^-	4866.6	3350.9
$\lvert 12;02\rangle - \lvert 02;12\rangle$	0,2,4	$B_2{}^+$	4852.2	3345.3
	1,3	$A_1{}^+$		
$\lvert 12;02\rangle + \lvert 02;12\rangle$	0,2,4	$A_1{}^+$		
	1,3	$B_2{}^+$		
$\lvert 13;00\rangle, \lvert 00;13\rangle$	3	E^-	4831.3	3338.2
$\lvert 11;02\rangle, \lvert 02;11\rangle$	1,2,3	E^-	4628.1	3230.3
$\lvert 01;12\rangle, \lvert 12;01\rangle$	1,2,3	E^-	4616.3	3226.1
$\lvert 10;02\rangle - \lvert 02;10\rangle$	2	$B_2{}^+$	4515.5	3172.6
$\lvert 10;02\rangle + \lvert 02;10\rangle$	2	$A_1{}^+$		
$\lvert 12;00\rangle - \lvert 00;12\rangle$	2	$B_2{}^+$	4497.8	3166.3
$\lvert 12;00\rangle + \lvert 00;12\rangle$	2	$A_1{}^+$		
$\lvert 11;01\rangle - \lvert 01;11\rangle$	0,2	$A_2{}^+$	4392.2	3111.1
	1	$B_1{}^+$		
$\lvert 11;01\rangle + \lvert 01;11\rangle$	0,2	$B_1{}^+$		
	1	$A_2{}^+$		
$\lvert 01;10\rangle, \lvert 10;01\rangle$	1	E^-	4279.6	3053.4
$\lvert 11;00\rangle, \lvert 00;11\rangle$	1	E^-	4273.7	3051.3
$\lvert 10;00\rangle - \lvert 00;10\rangle$	0	$B_2{}^+$	4161.1	2993.6
$\lvert 10;00\rangle + \lvert 00;10\rangle$	0	$A_1{}^+$		
$\lvert 02;00\rangle - \lvert 00;02\rangle$	2	$B_2{}^+$	354.0	179.1
$\lvert 02;00\rangle + \lvert 00;02\rangle$	2	$A_1{}^+$		
$\lvert 01;01\rangle$	0,2	$B_1{}^+$	237.0	119.6
	1	$A_2{}^+$		
$\lvert 01;00\rangle, \lvert 00;01\rangle$	1	E^-	118.5	59.8
$\lvert 00;00\rangle$	0	$A_1{}^+$	0.0	0.0

is built on the vibrational energy level structure in a rigid molecule. The $J = 0$ levels are obtained by combining each coarse level with (n, l) states having $l = j_{AB}$, the $J = 1$ levels by combining each coarse level with (n, l) states having $l = j_{AB} \pm 1$, and so on for higher J. Excluding spin effects only states of the same Γ_{rcv} in the MS group can perturb each other. The possible Γ_{coarse} are $A_1{}^+$ (para-para), $A_2{}^+$ (ortho-ortho), $B_1{}^+$ (ortho-ortho), $B_2{}^+$ (para-para), or E^- (ortho-para), and because of the symmetry properties of the $|n, l\rangle$ states this means that such perturbations will only be between states having the same Γ_{coarse} as well. As usual perturbations involving the nuclear spins can occur between any levels that have the same parity (given as + or − by the effect of E^*). The calculation of the hyperfine energy level splittings in $(H_2)_2$ is discussed by Verberne and Reuss (1981) and Schaefer (1994); we do not consider that problem here.

We consider the determination of the selection rules for allowed electric dipole transitions in $(H_2)_2$ and $(D_2)_2$ using the general expansion of $\mu_s^{(1,\sigma)}$ given in Eq. (16-13). Each $\mu_s^{(1,\sigma)}$ transforms as the dipole representation Γ^*, which is B_1^- in $\boldsymbol{G}_{16}$, and so allowed transitions are connected by this species. Also classifying $\mu_s^{(1,\sigma)}$ in $\boldsymbol{K}$(spatial) we have the usual $\Delta J = 0, \pm 1$ selection rule. For diatomic molecules expansions are customarily made in terms of the bond length r rather than in terms of the normal coordinate Q so that Eq. (16-13) for a dimer of two diatomic molecules becomes:

$$\mu_s^{(1,\sigma)} = \sum_{\mathrm{P}} \mu_{\mathrm{P}}^{(s)}(R, r_{\mathrm{A}}, r_{\mathrm{B}}) F_{\mathrm{P};\sigma}(\phi_{\mathrm{A}}, \theta_{\mathrm{A}}, \phi_{\mathrm{B}}, \theta_{\mathrm{B}}, \phi, \theta), \tag{16-41}$$

where $\mathrm{P} = \lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\lambda_{\mathrm{R}}$ and

$$\begin{aligned} &F_{\mathrm{P};\sigma}(\phi_{\mathrm{A}}, \theta_{\mathrm{A}}, \phi_{\mathrm{B}}, \theta_{\mathrm{B}}, \phi, \theta) \\ &\quad = \sum_{\Gamma} (-1)^{\lambda_{\mathrm{A}}-\lambda_{\mathrm{B}}+\sigma_{\mathrm{AB}}} \sqrt{2\lambda_{\mathrm{AB}}+1} \begin{pmatrix} \lambda_{\mathrm{A}} & \lambda_{\mathrm{B}} & \lambda_{\mathrm{AB}} \\ \sigma_{\mathrm{A}} & \sigma_{\mathrm{B}} & -\sigma_{\mathrm{AB}} \end{pmatrix} \\ &\quad \times (-1)^{\lambda_{\mathrm{AB}}-\lambda_{\mathrm{R}}+\sigma} \sqrt{3} \begin{pmatrix} \lambda_{\mathrm{AB}} & \lambda_{\mathrm{R}} & 1 \\ \sigma_{\mathrm{AB}} & \sigma_{\mathrm{R}} & -\sigma \end{pmatrix} \\ &\quad \times [D_{\sigma_{\mathrm{A}}0}^{(\lambda_{\mathrm{A}})}(\phi_{\mathrm{A}}, \theta_{\mathrm{A}}, 0)]^* [D_{\sigma_{\mathrm{B}}0}^{(\lambda_{\mathrm{B}})}(\phi_{\mathrm{B}}, \theta_{\mathrm{B}}, 0)]^* [D_{\sigma_{\mathrm{R}}0}^{(\lambda_{\mathrm{R}})}(\phi, \theta, 0)]^*, \end{aligned} \tag{16-42}$$

with $\Gamma = \sigma_{\mathrm{A}}, \sigma_{\mathrm{B}}, \sigma_{\mathrm{R}}, \sigma_{\mathrm{AB}}$.

As an aside to the symmetry analysis of the dipole moment expansion it should be mentioned that Meyer, Frommhold and Birnbaum (1989) (called MFB) have made an *ab initio* calculation of the dipole moment of $(H_2)_2$ over a grid of relative moiety orientations and intermoiety distances, with the H–H bond lengths fixed at the zero-point value r_0. The dipole moment is induced by intermoiety interaction. By least squares fitting MFB show that eight terms in the sum in Eq. (16-41) are significant for the H_2 dimer. The eight $\mu_{\mathrm{P}}^{(s)}(R, r_0, r_0)$, called $B_c(R)$ in MFB, that are significant are found to be (the symmetry properties of the terms are discussed below):

$$\begin{aligned} &B_{2021}(R) = -B_{0221}(R), B_{2023}(R) = -B_{0223}(R), \\ &B_{2211}(R), B_{2233}(R), \text{and } B_{4045}(R) = -B_{0445}(R), \end{aligned} \tag{16-43}$$

where the subscript c on B is $\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\lambda_{\mathrm{R}}$ (called $\lambda_1\lambda_2\Lambda L$ in MFB). At $R = 6a_0$ the *ab initio* value of the dipole moment for the T-shaped configuration[4] is calculated to be 0.027 D (9.0×10^{-32} C m), and at all orientations the dominating contribution is the quadrupole induced term ($\lambda_{\mathrm{AB}}\lambda_{\mathrm{R}} = 23$). MFB found that the $B_c(R)$ can be fitted to the analytical expansion:

$$B_c(R) = \frac{B_c^{(n)}}{R^n} + B_c^{(0)}\exp[a_c(R - R_0) + b_c(R - R_0)^2], \tag{16-44}$$

---

[4] **This configuration has the largest value for the induced dipole moment.**

where $R_0=6a_0$ is fixed, and $B_c^{(n)}$, $B_c^{(0)}$, a_c and b_c are determined in a least squares fitting with n fixed at the value appropriate for the leading term [4 for $c = 2023$ and 2233, 6 for $c = 4045$, and 7 for $c = 2021$ and 2211; see Eq. (20) and the discussion following it in MFB]. The accuracy of this *ab initio* calculation of the dipole moment is assessed in MFB to be of the order of 1%.

Returning to the symmetry analysis, we can use $\boldsymbol{G}_{16}$ to determine which $\mu_{\mathrm{P}}^{(s)}(R, r_{\mathrm{A}}, r_{\mathrm{B}})$ are nonvanishing, and from these results the selection rules for allowed electric dipole transitions follow. In order to obtain coefficients that transform irreducibly in the MS group we write

$$\begin{aligned}\mu_{\mathrm{P}}^{(s)}(R, r_{\mathrm{A}}, r_{\mathrm{B}}) = \sum_{n_1 \geq n_2} [&\mu^{(+)}_{\mathrm{P}n_1n_2}(R)c^{(+)}_{n_1n_2}(r_{\mathrm{A}}, r_{\mathrm{B}}) \\ &+ \mu^{(-)}_{\mathrm{P}n_1n_2}(R)c^{(-)}_{n_1n_2}(r_{\mathrm{A}}, r_{\mathrm{B}})],\end{aligned} \qquad (16\text{-}45)$$

where

$$c^{(\pm)}_{n_1n_2}(r_{\mathrm{A}}, r_{\mathrm{B}}) = [(\Delta r_{\mathrm{A}})^{n_1}(\Delta r_{\mathrm{B}})^{n_2} \pm (\Delta r_{\mathrm{A}})^{n_2}(\Delta r_{\mathrm{B}})^{n_1}], \qquad (16\text{-}46)$$

$n_1, n_2 = 0, 1, 2, \ldots$, $\Delta r = r - r_e$, and $c^{(+)}_{00}(r_{\mathrm{A}}, r_{\mathrm{B}}) = 1$. The $c^{(+)}_{n_1n_2}(r_{\mathrm{A}}, r_{\mathrm{B}})$ transform as $A_1{}^+$ and the $c^{(-)}_{n_1n_2}(r_{\mathrm{A}}, r_{\mathrm{B}})$ (which only exist for $n_1 \neq n_2$) transform as $B_2{}^+$. Since $\mu_s^{(1,\sigma)}$ is of symmetry $B_1{}^-$ the only nonvanishing $\mu^{(+)}_{\mathrm{P}n_1n_2}(R)$ are those that occur in Eq. (16-41) as coefficients of $F_{\mathrm{P};\sigma}$ functions having symmetry $B_1{}^-$, and the only nonvanishing $\mu^{(-)}_{\mathrm{P}n_1n_2}(R)$ are those that occur as coefficients of $F_{\mathrm{P};\sigma}$ functions having symmetry $A_2{}^-$. Terms with $n_1n_2 = 00$ give rise to transitions within the vibrational ground states of the moieties, and terms with $n_1n_2 = 10$ give rise to transitions in which one H_2 moiety stretching vibrational quantum number changes by one unit (in the harmonic oscillator approximation).

We have to determine which $F_{\mathrm{P};\sigma}$ functions are of symmetry $B_1{}^-$, and which are of symmetry $A_2{}^-$, in order to determine which $\mu^{(\pm)}_{\mathrm{P}n_1n_2}(R)$ are nonvanishing. The $F_{\mathrm{P};\sigma}$ functions transform like the angular basis functions[5] $|j_{\mathrm{A}}j_{\mathrm{B}}\pm\rangle|l\rangle$ given in Eqs. (16-34) and (16-35), and we can use the results in Table 16-2 to determine their symmetries. Functions $|j_{\mathrm{A}}j_{\mathrm{B}}\pm\rangle|l\rangle$ of symmetry $B_1{}^-$ are $|j_{\mathrm{A}}j_{\mathrm{B}}-\rangle|l\rangle$ functions, and those of symmetry $A_2{}^-$ are $|j_{\mathrm{A}}j_{\mathrm{B}}+\rangle|l\rangle$ functions; in each case they must have j_{A} and j_{B} even and l odd. Thus nonvanishing $\mu^{(\pm)}_{\mathrm{P}n_1n_2}(R)$ have λ_{A} and λ_{B} even, and λ_{R} odd; if $\lambda_{\mathrm{A}} = \lambda_{\mathrm{B}}$ then λ_{AB} must be odd for nonvanishing $\mu^{(+)}_{\mathrm{P}n_1n_2}(R)$, whereas λ_{AB} must be even for nonvanishing $\mu^{(-)}_{\mathrm{P}n_1n_2}(R)$. Because of the '−' sign in $|j_{\mathrm{A}}j_{\mathrm{B}}-\rangle|l\rangle$ having symmetry $B_1{}^-$, and the '+' sign in $|j_{\mathrm{A}}j_{\mathrm{B}}+\rangle|l\rangle$ having symmetry $A_2{}^-$, we have the relation

$$\mu^{(+)}_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\lambda_{\mathrm{R}}n_1n_2}(R) = -\mu^{(+)}_{\lambda_{\mathrm{B}}\lambda_{\mathrm{A}}\lambda_{\mathrm{AB}}\lambda_{\mathrm{R}}n_1n_2}(R), \qquad (16\text{-}47)$$

---

[5] In Eq. (11-19) the relation between the $[D^{(j)}_{m0}(\phi, \theta, 0)]^*$ functions and the spherical harmonic functions is given.

used in Eq. (16-43) above, and the relation

$$\mu^{(-)}_{\lambda_A\lambda_B\lambda_{AB}\lambda_R n_1 n_2}(R) = +\mu^{(-)}_{\lambda_B\lambda_A\lambda_{AB}\lambda_R n_1 n_2}(R). \tag{16-48}$$

For the $3j$ symbols in an $F_{P;\sigma}$ function to be nonvanishing we have the triangular[6] conditions $\Delta(\lambda_A\lambda_B\lambda_{AB})$ and $\Delta(\lambda_{AB}\lambda_R 1)$ which further restricts the possible values of λ_{AB} and λ_R according to

$$|\lambda_A - \lambda_B| \leq \lambda_{AB} \leq \lambda_A + \lambda_B, \tag{16-49}$$

and

$$|\lambda_{AB} - 1| \leq \lambda_R \leq \lambda_{AB} + 1. \tag{16-50}$$

Since λ_R is odd it follows that $\lambda_R = \lambda_{AB}$ if λ_{AB} is odd, and $\lambda_R = \lambda_{AB} \pm 1$ if λ_{AB} is even. In Table 16-4 we list nonvanishing $\mu^{(\pm)}_{Pn_1n_2}(R)$ for $(\lambda_A + \lambda_B) \leq 6$.

Table 16-4

Nonvanishing $\mu^{(\pm)}_{Pn_1n_2}(R)$ in Eq. (16-45) for $(\lambda_A + \lambda_B) \leq 6$.

λ_A	λ_B	λ_{AB}	λ_R	$(\pm)^a$	λ_A	λ_B	λ_{AB}	λ_R	$(\pm)^a$
0	0	0	1	(−)	2	2	0	1	(−)
0	2	2	1	(±)			1	1	(+)
			3	(±)			2	1	(−)
0	4	4	3	(±)				3	(−)
			5	(±)			3	3	(+)
0	6	6	5	(±)			4	3	(−)
			7	(±)				5	(−)
					2	4	2	1	(±)
								3	(±)
							3	3	(±)
							4	3	(±)
								5	(±)
							5	5	(±)
							6	5	(±)
								7	(±)

[a] The (±) indicates which $\mu^{(\pm)}_{Pn_1n_2}(R)$ is nonvanishing. For $\lambda_A \neq \lambda_B$ Eqs. (16-47) and (16-48) should also be used.

Forming matrix elements of $\mu_s^{(1,\sigma)}$ between the wavefunctions of Eqs. (16-32) to (16-35), and using Eq. (11-19) to write the spherical harmonic functions in terms of the $[D^{(j)}_{m0}(\phi, \theta, 0)]^*$ functions, we can use Eq. (14-23) to deduce the selection rules from the triangular conditions $\Delta(j'_A j''_A \lambda_A)$, $\Delta(j'_B j''_B \lambda_B)$ and

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[6] See Footnote 1 on page 563.

$\Delta(l'l''\lambda_R)$ required so that the $3j$ symbols arising from the use of of Eq. (14-23) are nonvanishing. We deduce that in allowed transitions Δj_A and Δj_B = even (i.e., ortho ↔ ortho, and para ↔ para only), and Δl = odd.

For a given 'coarse' transition we can determine the selection rules on l in more detail, and see which of the $\mu^{(\pm)}_{Pn_1n_2}(R)$ gives intensity to particular Δl transitions, by first determining the possible λ_A and λ_B from the triangular conditions $\Delta(j'_A j''_A \lambda_A)$, and $\Delta(j'_B j''_B \lambda_B)$. Then we look up in Table 16-4 the nonvanishing $\mu^{(\pm)}_{Pn_1n_2}(R)$ having these values of λ_A and λ_B. From the of λ_R of the $\mu^{(\pm)}_{Pn_1n_2}(R)$ one gets the selection rules on l. Two examples are discussed below; one has $|\Delta l| = 1, 3, 5$ and 7, and the other has only $|\Delta l| = 1$.

Since allowed rotation-contortion-vibration transitions are connected by B_1^- and have Δl odd, the allowed transitions can only be between 'coarse' states connected by B_2^+. Three types of 'band' are possible: (para,para) bands with coarse symmetry $A_1{}^+ \leftrightarrow B_2{}^+$, (ortho,para) bands with coarse symmetry $E^- \leftrightarrow E^-$, and (ortho,ortho) bands with coarse symmetry $A_2{}^+ \leftrightarrow B_1{}^+$.

For transitions originating in the ground vibrational states of both moieties [i.e., the transitions seen in absorption; see McKellar (1990), McKellar and Schaefer (1991) and references therein] a special notation is used to indicate Δj_A, v_A', j_A'', and Δj_B, v_B', j_B''; for example, we write $Q_1(1) + S_0(1)$ for the (ortho,ortho) band $(v'_A, j'_A; v'_B, j'_B) \leftarrow (v''_A, j''_A; v''_B, j''_B) = (1,1;0,3) \leftarrow (0,1;0,1)$. In this band, from the triangular conditions $\Delta(j'_A j''_A \lambda_A) = \Delta(11\lambda_A)$ and $\Delta(j'_B j''_B \lambda_B) = \Delta(13\lambda_B)$ we see that λ_A can be 0 or 2 and λ_B can be 2 or 4. Thus the $\mu^{(\pm)}_{Pn_1n_2}(R)$ having $(\lambda_A, \lambda_B) = (0,2), (0,4), (2,2)$ or $(2,4)$ can drive this transition and we can have $|\Delta l| = 1, 3, 5$ or 7. This result is also obtained from the general expression

$$|\Delta l| \leq j'_A + j'_B + j''_A + j''_B + 1 \tag{16-51}$$

which is derived in a straightforward manner from Eqs. (16-49) and (16-50) together with the triangular conditions $\Delta(l'l''\lambda_R)$, $\Delta(j'_A j''_A \lambda_A)$, and $\Delta(j'_B j''_B \lambda_B)$.

The $Q_1(0) + Q_0(0)$ band, i.e., $(|10;00\rangle - |00;10\rangle) \leftarrow |00;00\rangle$ [which derives its intensity from the term $\mu^{(-)}_{P10}(R) c^{(-)}_{10}(r_A, r_B) F_{P;\sigma}$ with $P = \lambda_A \lambda_B \lambda_{AB} \lambda_R = 0001$], only has $\Delta l = \pm 1$ fine structure. Pure Δl transitions in which there is no change in the coarse state are only possible for (ortho-para) coarse states of E^- symmetry (in the absence of nuclear spin coupling effects). However, the dipole moment of the (ortho-para) form of $(H_2)_2$ or $(D_2)_2$ associated with such transitions will be very small. Magnetic dipole transitions, as opposed to electric dipole transitions, are allowed between nuclear hyperfine components having the same parity (within a level of given J) and they have been observed by Verberne and Reuss (1980).

Examples of the three types of band seen in the spectrum are given in Table 16-5. From the statistical weights given in Eqs. (16-38) and (16-39), and the symmetry of the $|l\rangle$ wavefunctions given in Table 16-2, we determine that the three types of band have characteristically different intensity alternation

Table 16-5

Transition wavenumbers (in cm^{-1}) for $(H_2)_2$ and $(D_2)_2$.

$\Gamma'_{\mathrm{coarse}}$	$\Gamma''_{\mathrm{coarse}}$	Transition	$(H_2)_2$	$(D_2)_2$	$\lvert\Delta l\rvert$
B_2^+	A_1^+	$S_0(0) + Q_0(0)$	354.0	179.1	1,3
		$Q_1(0) + Q_0(0)$	4161.1	2993.6	1
		$S_1(0) + Q_0(0)$	4497.8	3166.3	1,3
		$Q_1(0) + S_0(0)$	4515.5	3172.6	1,3
		$S_1(0) + S_0(0)$	4852.2	3345.3	1,3,5
E^-	E^-	$Q_1(1) + Q_0(0)$	4155.2	2991.5	1,3
		$Q_0(1) + Q_1(0)$	4161.1	2993.6	1,3
		$Q_0(1) + S_1(0)$	4497.8	3166.3	1,3,5
		$Q_1(1) + S_0(0)$	4509.6	3170.5	1,3,5
		$S_1(1) + Q_0(0)$	4712.8	3278.4	1,3,5
		$S_0(1) + Q_1(0)$	4748.1	3291.1	1,3,5
B_1^+/A_2^+	A_2^+/B_1^+	$Q_1(1) + Q_0(1)$	4155.2	2991.5	1,3,5
		$S_1(1) + Q_0(1)$	4712.8	3278.4	1,3,5,7
		$Q_1(1) + S_0(1)$	4742.2	3288.9	1,3,5,7

with changing l value. In a $B_2^+ \leftrightarrow A_1^+$ band alternate lines are missing for $(H_2)_2$, and have a 7:5 intensity alternation for $(D_2)_2$. In a $B_1^+ \leftrightarrow A_2^+$ band there will be a 2:1 intensity alternation for $(H_2)_2$ and $(D_2)_2$, and in an $E^- \leftrightarrow E^-$ band there will be no intensity alternation for $(H_2)_2$ or $(D_2)_2$.

In Figs. 16-2 and 16-3 we give examples of absorption spectra of hydrogen and deuterium gas. In accordance with the selection rules derived above, there are $\Delta l = \pm 1$ and 3 transitions in the $S_1(0) + Q_0(0)$ band of $(H_2)_2$ in Fig. 16-2, but only $\Delta l = \pm 1$ transitions in the $Q_1(0) + Q_0(0)$ band of $(D_2)_2$ in Fig. 16-3. Fig. 16-2 shows clearly that only the $l = 0$ and 1 levels are sharp for $(H_2)_2$; higher l levels are rotationally predissociated. In Fig. 16-2 transitions from levels with odd l'' are missing, and in Fig. 16-3 we see the combined effect of the Boltzmann factor and the 7:5 intensity alternation for l'' = even:odd. More details of the infrared spectra of the hydrogen dimers are given in McKellar (1990).

The MS groups of the isotopomers $(HD)_2$, H_2-D_2 and H_2-HD are subgroups of the MS group $\boldsymbol{G}_{16}$ for $(H_2)_2$ and $(D_2)_2$. The MS group for H_2-D_2 happens to be identical to the CNPI group $\boldsymbol{G}_8$ of the hydrogen peroxide molecule; the character table is given in Table A-23 (we label the nuclei H_1H_2–D_3D_4). The MS groups for $(HD)_2$ and H_2-HD are isomorphic to each other, and the character tables are given in Table 16-6; we call the groups $\boldsymbol{G}_4$(HDHD) and $\boldsymbol{G}_4$(HHHD). To determine the implications of symmetry for $(HD)_2$, H_2-D_2 and

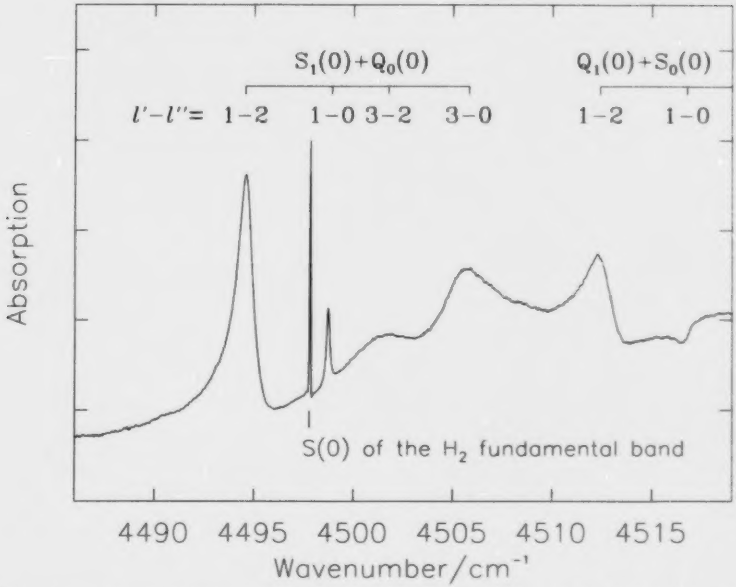

Fig. 16-2. Absorption spectrum due to para-H_2 in the region of the electric quadrupole $S(0)$ line of the $v = 1 \leftarrow 0$ band of the H_2 molecule. The $S_1(0)+Q_0(0)$ band, and a fragment of the $Q_1(0)+S_0(0)$ band, of the dimer are shown. This spectrum was taken by Dr. A. R. W. McKellar on a Bomem model DA3.02 Fourier transform spectrometer at a resolution of 0.04 cm^{-1}, with a hydrogen sample pressure of about 25 Torr, a sample temperature of about 20 K, and a path length of 112 m.

H_2-HD [and dimers such as $(CO)_2$, H_2-N_2 and H_2-CO] we use the correlation table, given in Table 16-7, in conjunction with the results given above (particularly Tables 16-1 and 16-2). A short discussion of some of the results is appropriate.

For $(HD)_2$ if one of j_A, j_B is even and the other odd then $|j_A j_B +\rangle$ is of symmetry A^- and $|j_A j_B -\rangle$ is of symmetry B^-. The statistical weights are given by

$$\Gamma^{\rm sw}_{\rm rve} = 15(A^+ \oplus A^-) \oplus 21(B^+ \oplus B^-). \qquad (16\text{-}52)$$

There will therefore be a 15:21 intensity alternation in the l structure of the 'bands'. Allowed rotation-contortion-vibration transitions are connected by A^-. There are four types of 'band' in the spectrum: two, with $\Gamma_{\rm coarse} = A^+ \leftrightarrow A^-$ or $B^+ \leftrightarrow B^-$ having Δl = even, and two with $\Gamma_{\rm coarse} = A^+ \leftrightarrow B^+$ or $A^- \leftrightarrow B^-$ having Δl = odd. The bands with Δl = even do not occur for $(H_2)_2$, $(D_2)_2$ or H_2-D_2, and will tend to be relatively weak; they may also be obscured by the dipole spectrum of the monomer.

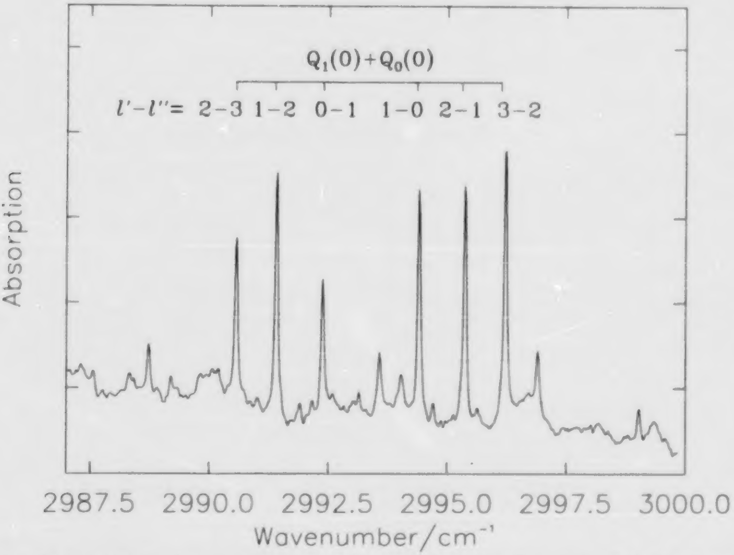

Fig. 16-3. Absorption spectrum due to para-D_2 in the Q region of the fundamental band. The $Q_1(0)+Q_0(0)$ band of the dimer is shown. This spectrum was taken by Dr. A. R. W. McKellar with the same apparatus and conditions as for Fig. 16-2, with a deuterium sample pressure of about 17 Torr.

Table 16-6

The groups G_4(HDHD) and G_4(HHHD) for $(HD)_2$ and H_2-HD[a].

G_4(HDHD) :	E	(13)(24)	E^*	$(13)(24)^*$
G_4(HHHD) :	E	(12)	E^*	$(12)^*$
A^+ :	1	1	1	1
A^- :	1	1	−1	−1
B^+ :	1	−1	1	−1
B^- :	1	−1	−1	1

[a] Nuclei labeled H_1D_2-H_3D_4 and H_1H_2-H_3D_4.

For H_2-D_2 and H_2-HD it is not appropriate to form basis functions having the ± combinations given in Eqs. (16-33) and (16-34) since the moieties are not identical. There cannot be any intensity alternation in the l structure.

For H_2-D_2 the symmetry of $|j(H_2)\rangle$ is A_1' or B_1'' as $j(H_2)$ is even or odd

Table 16-7

The correlation table for the irreducible representations.

G_{16}	G_8	G_4(HDHD)	G_4(HHHD)
A_1^+	A_1'	A^+	A^+
A_2^+	A_1''	B^+	B^+
B_1^+	A_1''	A^+	B^+
B_2^+	A_1'	B^+	A^+
E^+	$B_2' \oplus B_2''$	$A^+ \oplus B^+$	$A^+ \oplus B^+$
A_1^-	A_2''	A^-	B^-
A_2^-	A_2'	B^-	A^-
B_1^-	A_2'	A^-	A^-
B_2^-	A_2''	B^-	B^-
E^-	$B_1' \oplus B_1''$	$A^- \oplus B^-$	$A^- \oplus B^-$

respectively, and for $|j(D_2)\rangle$ it is A_1' or B_1' as $j(D_2)$ is even or odd respectively. The statistical weights are given by

$$\Gamma^{\text{sw}}_{\text{rve}} = 6(A_1' \oplus A_2') \oplus 9(A_1'' \oplus A_2'') \oplus 3(B_1' \oplus B_2') \oplus 18(B_1'' \oplus B_2''). \tag{16-53}$$

Allowed transitions are between rotation-contortion-vibration states whose symmetries are connected by A_2' with Δl = odd, and are between coarse states having the same Γ_{coarse} symmetry.

For H_2-HD the symmetry of $|j(H_2)\rangle$ is A^+ or B^- as $j(H_2)$ is even or odd respectively, and for $|j(\text{HD})\rangle$ it is A^+ or A^- as $j(\text{HD})$ is even or odd respectively. The statistical weights are given by

$$\Gamma^{\text{sw}}_{\text{rve}} = (A^+ \oplus A^-) \oplus 3(B^+ \oplus B^-). \tag{16-54}$$

Allowed transitions are between rotation-contortion-vibration states whose symmetries are connected by A^-.

16.5.2 The ammonia dimer

The second example of a weakly bound cluster molecule, the ammonia dimer, is described in a body fixed reference frame. The convention chosen for labeling the nuclei, and for defining the body fixed (x, y, z) axis system, is shown in Fig. 16-4. Moiety A is labeled $N_7H_1H_2H_3$, and moiety B is $N_8H_4H_5H_6$.

The polar nature of the ammonia dimer was discovered by Odutola, Dyke, Howard, and Muenter (1979) in a molecular beam electric deflection experiment. The dimer was believed to have a 'classical' hydrogen-bonded structure in which an NH bond of the donor moiety points towards the electron lone pair of the acceptor moiety in a linear or nearly linear N-H—N arrangement; the N-H—N direction being colinear with the three-fold symmetry axis of the acceptor moiety. The first spectrum of this molecule was obtained in the microwave region by Nelson, Fraser, and Klemperer (1985); the analysis of the spectrum contradicted this expectation about the hydrogen bond. In the years that followed many experimental and *ab initio* results have been published, and in the Bibliographical Notes we review this history. The (current) conclusion is that the equilibrium structure is roughly as depicted in Fig 16-4, and there is feasible internal rotation of each moiety about its C_3 axis. Also the barrier at the 'cyclic' C_{2h} transition state between two versions of the equilibrium structure (see Fig. 16-5) is hardly significantly different from zero, and this donor-acceptor interchange tunneling motion is very facile. For the HF dimer a similar tunneling motion occurs at a hydrogen bond (see Fig. 3-13), and it also occurs for the water dimer [see the degenerate rearrangement (1) ↔ (5) in Fig. 3-15]. However, for these two dimers the barrier to donor-acceptor interchange is about 300 cm^{-1}; significantly different from zero. If this were the full story about the feasible contortional tunneling motions in the ammonia dimer then the MS group would be the group G_{36} introduced earlier for torsionally tunneling ethane, dimethylacetylene and acetone (see Section 15.4.4 and Table A-28). However, in 1992 two experimental groups [Havenith, Linnartz, Zwart, Kips, ter Meulen, and Meerts (1992), and Loeser, Schmuttenmaer, Cohen, Elrod, Steyert, Saykally, Bumgarner, and Blake (1992)] discovered the presence of splittings in the spectrum of the ammonia dimer due to ammonia inversion. At the same time a theoretical paper by van Bladel, van der Avoird, Wormer, and Saykally (1992) argued that, based on the results of energy level calculations, the dimer spectrum obtained by Nelson, Fraser, and Klemperer (1985) could only be understood if ammonia moiety inversion were feasible. Allowing for the inversion of the ammonia moieties, the molecular symmetry group of the ammonia dimer is G_{144}; the character table of this group is given in Table A-30.

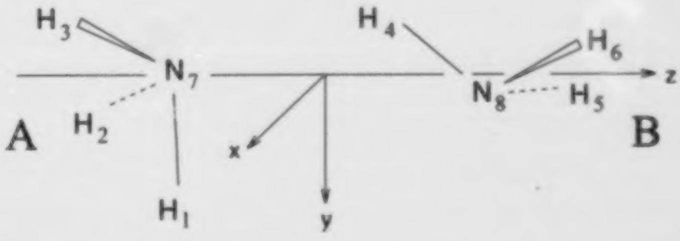

Fig. 16-4. The labeling of the nuclei and the body fixed axis system (x, y, z) used for the ammonia dimer. The z axis is defined so that it points from the center of mass of moiety A to the center of mass of moiety B, and the directions of the x and y axes are obtained by setting the Euler angle $\chi = 0$ (see Section 16.2.2).

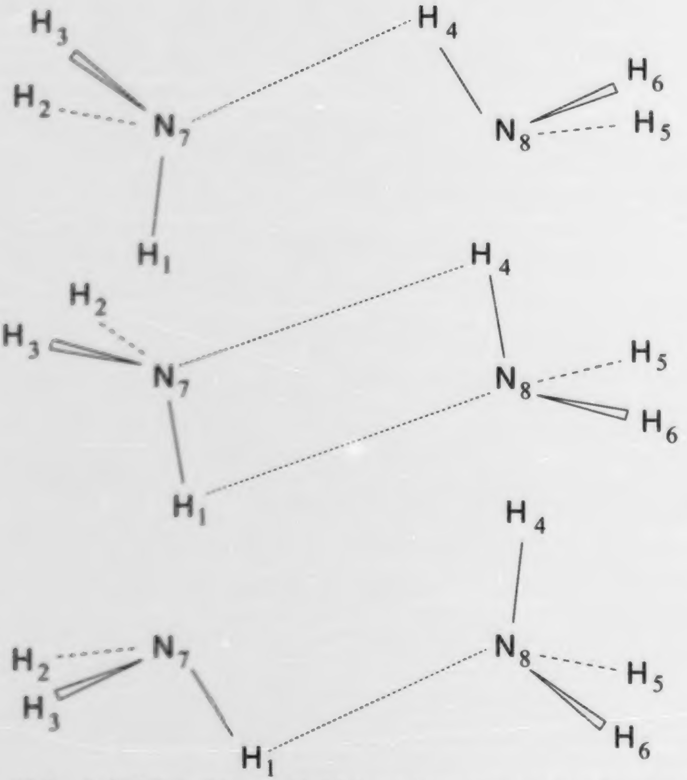

Fig. 16-5. A depiction of the weakly hindered donor-acceptor interchange motion of the ammonia dimer about the 'cyclic' C_{2h} structure.

The MS group G_{144} is large, and in the future as larger clusters become the subject of spectroscopic study it will undoubtedly become important to be able to handle large MS groups. We can use the ammonia dimer, and its MS group, as an example of the approach used. To determine the effects of the operations of a large MS group on the molecular coordinates, operators, and wavefunctions one need consider only the effects of generating operations of the group [see Eqs. (12-67) and (12-68)]. Further, the classification of basis functions in the group, and the determination of linear combinations that transform irreducibly, is best accomplished by making use of the product decomposition of the group (see Sections 5.7 and 5.8.2). Following van der Avoird, Wormer, and Moszynski (1994), we choose the six generating operations of G_{144} as (123), (456), (14)(25)(36)(78), (23)(56)*, (23), and (56). Following Olthof, van der Avoird, Wormer, Loeser, and Saykally (1994), we make use of the following product decomposition of $\boldsymbol{G}_{144}$:

$$\boldsymbol{G}_{144} = (\boldsymbol{G}^{\mathrm{g}}_{3\mathrm{v}} \otimes \boldsymbol{G}^{\mathrm{ag}}_{3\mathrm{v}} \otimes \{E, E^*\}) \circledS \{E, (56)\}. \tag{16-55}$$

This involves direct and semidirect products (see Section 5.7) and we will explain the notation for the subgroups and the way this product decomposition is used below. But first we show how to determine the transformation properties of the molecular coordinates in the group by using generating operations.

We initially consider the transformation properties of the coordinates describing the intermoiety stretch, the end-over-end rotation, and the moiety rotation under the effect of the generating operations of $\boldsymbol{G}_{144}$. Since we are using a body fixed reference frame, these coordinates are R, the distance between the centers of mass of the moieties, θ and ϕ, the two Euler angles specifying the direction of the body fixed z axis relative to a space fixed axis system, and the two sets of body fixed Euler angles $(\theta^{\mathrm{m}}_{\mathrm{A}}, \phi^{\mathrm{m}}_{\mathrm{A}}, \chi^{\mathrm{m}}_{\mathrm{A}})$ and $(\theta^{\mathrm{m}}_{\mathrm{B}}, \phi^{\mathrm{m}}_{\mathrm{B}}, \chi^{\mathrm{m}}_{\mathrm{B}})$. For each moiety M (= A or B) we define a moiety fixed axis system $(x_{\mathrm{M}}, y_{\mathrm{M}}, z_{\mathrm{M}})$. For moiety A, this axis system is defined exactly as described for an isolated ammonia molecule in Section 15.4.1 [in particular, see Fig. 15-2], and for moiety B it is defined analogously with H_1, H_2 and H_3 replaced by H_4, H_5 and H_6, respectively.

It is important to appreciate that the body fixed Euler angles $(\theta^{\mathrm{m}}_{\mathrm{M}}, \phi^{\mathrm{m}}_{\mathrm{M}}, \chi^{\mathrm{m}}_{\mathrm{M}})$, M = A or B, define the orientation of the $(x_{\mathrm{M}}, y_{\mathrm{M}}, z_{\mathrm{M}})$ axes relative to the body fixed axes (x, y, z). This has important implications when we determine the effect of MS group operations on $(\theta^{\mathrm{m}}_{\mathrm{M}}, \phi^{\mathrm{m}}_{\mathrm{M}}, \chi^{\mathrm{m}}_{\mathrm{M}})$. So far we have used Euler angles (θ, ϕ, χ) to specify the orientation of a molecule fixed (or body fixed) (x, y, z) axis system relative to the space fixed (ξ, η, ζ) axes [see Fig. 10-1]. In this situation, operations in the MS group affect only the (x, y, z) axes; they leave the (ξ, η, ζ) axes unchanged and the transformation properties of (θ, ϕ, χ) can be determined as described in Section 12.1. However, when we derive the MS group transformation properties of the $(\theta^{\mathrm{m}}_{\mathrm{M}}, \phi^{\mathrm{m}}_{\mathrm{M}}, \chi^{\mathrm{m}}_{\mathrm{M}})$ angles some MS group operations affect both the $(x_{\mathrm{M}}, y_{\mathrm{M}}, z_{\mathrm{M}})$ *and* the (x, y, z) axes. The (x, y, z) axes are affected by MS group operations that interchange the centers of mass of the two moieties. The generating operations (14)(25)(36)(78) and (23)(56)* have this effect for the NH_3 dimer. They reverse the orientation of the body fixed z axis so that θ and ϕ transform according to

$$(\theta, \phi) \rightarrow (\pi - \theta, \pi + \phi). \tag{16-56}$$

Thus after one of these symmetry operations has been applied to the molecule, the orientation of the body fixed axes (x, y, z) relative to the space fixed axes (ξ, η, ζ) is described by the Euler angles $(\pi - \theta, \pi + \phi, \chi = 0)$; the (x, y, z) axis system is rotated by π about the x axis. Further geometrical arguments [consider Fig. 10-1 with (x, y, z) renamed to $(x_{\mathrm{M}}, y_{\mathrm{M}}, z_{\mathrm{M}})$ and (ξ, η, ζ) renamed to (x, y, z)] show a hypothetical symmetry operation that leaves the orientation of the $(x_{\mathrm{M}}, y_{\mathrm{M}}, z_{\mathrm{M}})$ axis system in space unchanged, but which rotates the (x, y, z) axis system by π about the x axis, to have the effect

$$(\theta^{\mathrm{m}}_{\mathrm{M}}, \phi^{\mathrm{m}}_{\mathrm{M}}, \chi^{\mathrm{m}}_{\mathrm{M}}) \rightarrow (\pi - \theta^{\mathrm{m}}_{\mathrm{M}}, 2\pi - \phi^{\mathrm{m}}_{\mathrm{M}}, \pi + \chi^{\mathrm{m}}_{\mathrm{M}}). \tag{16-57}$$

For elements of the MS group that affect both the $(x_{\mathrm{M}}, y_{\mathrm{M}}, z_{\mathrm{M}})$ and the (x, y, z) axis systems, we determine first the effect on $(\theta^{\mathrm{m}}_{\mathrm{M}}, \phi^{\mathrm{m}}_{\mathrm{M}}, \chi^{\mathrm{m}}_{\mathrm{M}})$ of the change in $(x_{\mathrm{M}}, y_{\mathrm{M}}, z_{\mathrm{M}})$ by employing the ideas of Section 12.1, and we then use Eq. (16-57) to obtain the effect of the change in the (x, y, z) axes.

The transformation properties of the various coordinates [including ρ_{A} and ρ_{B}, the inversion angles of the two moieties; see Section 15.4.1] under the generating operations of $\boldsymbol{G}_{144}$ are given in Table 16-8. The operations (123), (456), (23), and (56) do not affect the (x, y, z) axes and the transformation properties of the $(\theta^{\mathrm{m}}_{\mathrm{M}}, \phi^{\mathrm{m}}_{\mathrm{M}}, \chi^{\mathrm{m}}_{\mathrm{M}})$ can be determined as described in Section 12.1. The operation (14)(25)(36)(78) initially causes the two sets of body fixed Euler angles to be interchanged: $(\theta^{\mathrm{m}}_{\mathrm{A}}, \phi^{\mathrm{m}}_{\mathrm{A}}, \chi^{\mathrm{m}}_{\mathrm{A}}) \leftrightarrow (\theta^{\mathrm{m}}_{\mathrm{B}}, \phi^{\mathrm{m}}_{\mathrm{B}}, \chi^{\mathrm{m}}_{\mathrm{B}})$. This operation reverses the z axis and we must apply Eq. (16-57) to the interchanged angles to account for the resulting effect. The effect of the operation $(23)(56)^*$ on the moiety fixed axis systems $(x_{\mathrm{M}}, y_{\mathrm{M}}, z_{\mathrm{M}})$, M = A or B, is described by the equivalent rotation $R_{\pi/2}{}^{\pi}$ [a rotation of π about the y_{M} axis]. The equivalent rotation causes the change [see Table 12-1]

$$(\theta^{\mathrm{m}}_{\mathrm{M}}, \phi^{\mathrm{m}}_{\mathrm{M}}, \chi^{\mathrm{m}}_{\mathrm{M}}) \rightarrow (\pi - \theta^{\mathrm{m}}_{\mathrm{M}}, \pi + \phi^{\mathrm{m}}_{\mathrm{M}}, \pi - \chi^{\mathrm{m}}_{\mathrm{M}}). \tag{16-58}$$

However, $(23)(56)^*$ also reverses the z axis and we must apply Eq. (16-57) to the result of Eq. (16-58) to obtain the transformation properties in Table 16-8.

Table 16-8

The transformation properties of the coordinates in $\boldsymbol{G}_{144}$.

E	(123)	(456)	(14)(25)(36)(78)	$(23)(56)^*$	(23)	(56)
$\theta^{\mathrm{m}}_{\mathrm{A}}$	$\theta^{\mathrm{m}}_{\mathrm{A}}$	$\theta^{\mathrm{m}}_{\mathrm{A}}$	$\pi - \theta^{\mathrm{m}}_{\mathrm{B}}$	$\theta^{\mathrm{m}}_{\mathrm{A}}$	$\pi - \theta^{\mathrm{m}}_{\mathrm{A}}$	$\theta^{\mathrm{m}}_{\mathrm{A}}$
$\phi^{\mathrm{m}}_{\mathrm{A}}$	$\phi^{\mathrm{m}}_{\mathrm{A}}$	$\phi^{\mathrm{m}}_{\mathrm{A}}$	$2\pi - \phi^{\mathrm{m}}_{\mathrm{B}}$	$\pi - \phi^{\mathrm{m}}_{\mathrm{A}}$	$\pi + \phi^{\mathrm{m}}_{\mathrm{A}}$	$\phi^{\mathrm{m}}_{\mathrm{A}}$
$\chi^{\mathrm{m}}_{\mathrm{A}}$	$\chi^{\mathrm{m}}_{\mathrm{A}} - 2\pi/3$	$\chi^{\mathrm{m}}_{\mathrm{A}}$	$\pi + \chi^{\mathrm{m}}_{\mathrm{B}}$	$2\pi - \chi^{\mathrm{m}}_{\mathrm{A}}$	$2\pi - \chi^{\mathrm{m}}_{\mathrm{A}}$	$\chi^{\mathrm{m}}_{\mathrm{A}}$
$\theta^{\mathrm{m}}_{\mathrm{B}}$	$\theta^{\mathrm{m}}_{\mathrm{B}}$	$\theta^{\mathrm{m}}_{\mathrm{B}}$	$\pi - \theta^{\mathrm{m}}_{\mathrm{A}}$	$\theta^{\mathrm{m}}_{\mathrm{B}}$	$\theta^{\mathrm{m}}_{\mathrm{B}}$	$\pi - \theta^{\mathrm{m}}_{\mathrm{B}}$
$\phi^{\mathrm{m}}_{\mathrm{B}}$	$\phi^{\mathrm{m}}_{\mathrm{B}}$	$\phi^{\mathrm{m}}_{\mathrm{B}}$	$2\pi - \phi^{\mathrm{m}}_{\mathrm{A}}$	$\pi - \phi^{\mathrm{m}}_{\mathrm{B}}$	$\phi^{\mathrm{m}}_{\mathrm{B}}$	$\pi + \phi^{\mathrm{m}}_{\mathrm{B}}$
$\chi^{\mathrm{m}}_{\mathrm{B}}$	$\chi^{\mathrm{m}}_{\mathrm{B}}$	$\chi^{\mathrm{m}}_{\mathrm{B}} - 2\pi/3$	$\pi + \chi^{\mathrm{m}}_{\mathrm{A}}$	$2\pi - \chi^{\mathrm{m}}_{\mathrm{B}}$	$\chi^{\mathrm{m}}_{\mathrm{B}}$	$2\pi - \chi^{\mathrm{m}}_{\mathrm{B}}$
θ	θ	θ	$\pi - \theta$	$\pi - \theta$	θ	θ
ϕ	ϕ	ϕ	$\pi + \phi$	$\pi + \phi$	ϕ	ϕ
R	R	R	R	R	R	R
ρ_{A}	ρ_{A}	ρ_{A}	ρ_{B}	ρ_{A}	$\pi - \rho_{\mathrm{A}}$	ρ_{A}
ρ_{B}	ρ_{B}	ρ_{B}	ρ_{A}	ρ_{B}	ρ_{B}	$\pi - \rho_{\mathrm{B}}$

We now determine the symmetry restrictions imposed by the MS group on the expansion of the potential energy function $V^{(\mathrm{m})}_{\mathrm{int}}$ in Eq. (16-12), and on the expansion of the body fixed dipole moment components $\mu_{\mathrm{m}}^{(1,\sigma')}$ in Eq. (16-16). In both cases, we expand in angle-dependent functions

$$
\begin{aligned}
&A_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{A}}\sigma'_{\mathrm{B}};\sigma'}(\theta_{\mathrm{A}}^{\mathrm{m}},\phi_{\mathrm{A}}^{\mathrm{m}},\chi_{\mathrm{A}}^{\mathrm{m}},\theta_{\mathrm{B}}^{\mathrm{m}},\phi_{\mathrm{B}}^{\mathrm{m}},\chi_{\mathrm{B}}^{\mathrm{m}})\\
&=\sum_{\sigma_{\mathrm{A}},\sigma_{\mathrm{B}}}\begin{pmatrix}\lambda_{\mathrm{A}} & \lambda_{\mathrm{B}} & \lambda_{\mathrm{AB}}\\ \sigma_{\mathrm{A}} & \sigma_{\mathrm{B}} & -\sigma'\end{pmatrix}\\
&\times[D^{(\lambda_{\mathrm{A}})}_{\sigma_{\mathrm{A}}\sigma'_{\mathrm{A}}}(\phi_{\mathrm{A}}^{\mathrm{m}},\theta_{\mathrm{A}}^{\mathrm{m}},\chi_{\mathrm{A}}^{\mathrm{m}})]^*[D^{(\lambda_{\mathrm{B}})}_{\sigma_{\mathrm{B}}\sigma'_{\mathrm{B}}}(\phi_{\mathrm{B}}^{\mathrm{m}},\theta_{\mathrm{B}}^{\mathrm{m}},\chi_{\mathrm{B}}^{\mathrm{m}})]^* \qquad (16\text{-}59)
\end{aligned}
$$

and we initially derive the transformation properties of these functions. That is, we insert the transformed coordinates from Table 16-8 and use the transformation properties of the $D^{(\lambda)*}_{\sigma\sigma'}$ functions [see Section 3.5 of Zare (1988)] to simplify the expressions obtained. The results are given in Table 16-9. For later use, we give in the table also the transformation properties of the function $S_{Jkm}(\theta,\phi)$ [Eq. (11-16)] entering into Eq. (16-24). These transformation properties are straightforwardly determined from the transformation properties of θ and ϕ in Table 16-8 and the results of Section 12.1.

Table 16-9

The transformation properties of the functions $A_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{A}}\sigma'_{\mathrm{B}};\sigma'}$ [Eq. (16-59)] and $S_{Jkm}(\theta,\phi)$ [Eq. (11-16)] in G_{144}.

R	$RA_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{A}}\sigma'_{\mathrm{B}};\sigma'}$	RS_{Jkm}
(123)	$e^{-i\sigma'_{\mathrm{A}}\omega}A_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{A}}\sigma'_{\mathrm{B}};\sigma'}$	S_{Jkm}
(456)	$e^{-i\sigma'_{\mathrm{B}}\omega}A_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{A}}\sigma'_{\mathrm{B}};\sigma'}$	S_{Jkm}
(14)(25)(36)(78)	$(-1)^{\lambda_{\mathrm{A}}+\lambda_{\mathrm{B}}}A_{\lambda_{\mathrm{B}}\lambda_{\mathrm{A}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{B}}\sigma'_{\mathrm{A}};-\sigma'}$	$(-1)^J S_{J-km}$
(23)(56)*	$(-1)^{\lambda_{\mathrm{A}}+\lambda_{\mathrm{B}}+\lambda_{\mathrm{AB}}+\sigma'_{\mathrm{A}}+\sigma'_{\mathrm{B}}}A_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}-\sigma'_{\mathrm{B}}-\sigma'_{\mathrm{A}};-\sigma'}$	$(-1)^J S_{J-km}$
(23)	$(-1)^{\lambda_{\mathrm{A}}}A_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}-\sigma'_{\mathrm{A}}\sigma'_{\mathrm{B}};\sigma'}$	S_{Jkm}
(56)	$(-1)^{\lambda_{\mathrm{B}}}A_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{A}}-\sigma'_{\mathrm{B}};\sigma'}$	S_{Jkm}

$\omega = 2\pi/3$.

In terms of the functions $A_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{AB}}\sigma'_{\mathrm{A}}\sigma'_{\mathrm{B}};\sigma'}$, the intermolecular potential energy function $V_{\mathrm{int}}^{(\mathrm{m})}$ [Eq. (16-12)] is given by

$$
\begin{aligned}
V_{\mathrm{int}}^{(\mathrm{m})} = &\sum_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{R}}k_{\mathrm{A}}k_{\mathrm{B}}} V_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{R}}k_{\mathrm{A}}k_{\mathrm{B}}}(R,\rho_{\mathrm{A}},Q_{r_{\mathrm{A}}},\rho_{\mathrm{B}},Q_{r_{\mathrm{B}}})\\
&\times A_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{R}}k_{\mathrm{A}}k_{\mathrm{B}};0}(\theta_{\mathrm{A}}^{\mathrm{m}},\phi_{\mathrm{A}}^{\mathrm{m}},\chi_{\mathrm{A}}^{\mathrm{m}},\theta_{\mathrm{B}}^{\mathrm{m}},\phi_{\mathrm{B}}^{\mathrm{m}},\chi_{\mathrm{B}}^{\mathrm{m}}). \qquad (16\text{-}60)
\end{aligned}
$$

We have changed the notation slightly relative to Eq. (16-12). For the ammonia dimer, we indicate explicitly that the expansion function $V_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda_{\mathrm{R}}k_{\mathrm{A}}k_{\mathrm{B}}}$ depends not only on the normal coordinates Q_{r_A} and Q_{r_B} describing the vibrational motion of the two moieties, but also on on ρ_A and ρ_B, the two angles describing the large-amplitude inversion motion [the moiety *contortion*, see Section 15.4.1]. The potential $V_{\text{int}}^{(m)}$ is invariant to the operations in the MS group G_{144}. It follows from Table 16-9 that invariance under the generating operation (123) requires the condition:

$$\begin{aligned}V_{\lambda_A\lambda_B\lambda_R k_A k_B}&(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B})\\ &= e^{-ik_A\omega}\, V_{\lambda_A\lambda_B\lambda_R k_A k_B}(R, \rho_A, Q'_{r_A}, \rho_B, Q_{r_B})\end{aligned} \tag{16-61}$$

to be satisfied, where $Q'_{r_A} = (123)Q_{r_A}$ and $\omega = 2\pi/3$. Similarly, invariance under (456) requires

$$\begin{aligned}V_{\lambda_A\lambda_B\lambda_R k_A k_B}&(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B})\\ &= e^{-ik_B\omega}\, V_{\lambda_A\lambda_B\lambda_R k_A k_B}(R, \rho_A, Q_{r_A}, \rho_B, Q'_{r_B})\end{aligned} \tag{16-62}$$

where $Q'_{r_B} = (456)Q_{r_B}$. If we take the moieties to be semirigid [by setting all $Q_{r_A} = Q'_{r_A} = 0$ and all $Q_{r_B} = Q'_{r_B} = 0$ in Eqs. (16-61) and (16-62), but letting ρ_A and ρ_B vary], then only expansion functions with $k_A = 3t_A$ and $k_B = 3t_B$, where t_A and t_B are integers, would be nonvanishing. If the moieties were allowed to be nonrigid, then more expansion functions would be nonvanishing. For example, each of the ammonia moieties has degenerate normal coordinates $(Q_{ta}^{(M)}, Q_{tb}^{(M)})$, M = A or B, for which the linear combinations $Q_t{}^{(M)\pm} = Q_{ta}^{(M)} \pm iQ_{tb}^{(M)}$ can be chosen to transform as

$$(123)Q_t{}^{(A)\pm} = e^{\mp i\omega}Q_t{}^{(A)\pm} \text{ and } (456)Q_t{}^{(B)\pm} = e^{\mp i\omega}Q_t{}^{(B)\pm} \tag{16-63}$$

as described for CH_3F in Table 12-4. An expansion function of the form

$$\begin{aligned}V_{\lambda_A\lambda_B\lambda_R k_A k_B}&(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B})\\ &= \sum_t c^{(t)}_{\lambda_A\lambda_B\lambda_R k_A k_B}(R, \rho_A, \rho_B)\, Q_t{}^{(A)-}\end{aligned} \tag{16-64}$$

will fulfill Eq. (16-61) for $k_A = 1 + 3t_A$, and a linear combination of the $Q_t{}^{(A)+}$ will produce nonvanishing expansion functions with $k_A = 2 + 3t_A$. Clearly we can form analogous functions with $k_B = 1 + 3t_B$ and $k_B = 2 + 3t_B$.

Further, invariance under (14)(25)(36)(78) imposes the condition:

$$\begin{aligned}V_{\lambda_B\lambda_A\lambda_R k_B k_A}&(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B})\\ &= (-1)^{\lambda_A+\lambda_B}\, V_{\lambda_A\lambda_B\lambda_R k_A k_B}(R, \rho_B, Q_{r_B}, \rho_A, Q_{r_A}),\end{aligned} \tag{16-65}$$

and invariance under (23)(56)*, (23), and (56) requires

$$\begin{aligned}V_{\lambda_A\lambda_B\lambda_R -k_A -k_B}&(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B})\\ &= (-1)^{\lambda_A+\lambda_B+\lambda_R+k_A+k_B}\, V_{\lambda_A\lambda_B\lambda_R k_A k_B}(R, \rho_A, Q'_{r_A}, \rho_B, Q'_{r_B})\end{aligned} \tag{16-66}$$

with $Q'_{r_A} = (23)^* Q_{r_A}$ and $Q'_{r_B} = (56)^* Q_{r_B}$,

$$V_{\lambda_A \lambda_B \lambda_R -k_A k_B}(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B}) \\ = (-1)^{\lambda_A} V_{\lambda_A \lambda_B \lambda_R k_A k_B}(R, \pi - \rho_A, Q'_{r_A}, \rho_B, Q_{r_B}) \tag{16-67}$$

with $Q'_{r_A} = (23) Q_{r_A}$, and

$$V_{\lambda_A \lambda_B \lambda_R k_A -k_B}(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B}) \\ = (-1)^{\lambda_B} V_{\lambda_A \lambda_B \lambda_R k_A k_B}(R, \rho_A, Q_{r_A}, \pi - \rho_B, Q'_{r_B}) \tag{16-68}$$

with $Q'_{r_B} = (56) Q_{r_B}$.

The body fixed dipole moment components $\mu_{\mathrm{m}}^{(1,\sigma')}$ [Eq. (16-16)] can be expressed as

$$\mu_{\mathrm{m}}^{(1,\sigma')} = \sum_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A \sigma'_B} \mu^{(\mathrm{m})}_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A \sigma'_B, \sigma'}(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B}) (-1)^{\lambda_A - \lambda_B + \sigma'} \\ \times \sqrt{2\lambda_{AB} + 1}\, A_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A \sigma'_B ; \sigma'}(\theta_A^{\mathrm{m}}, \phi_A^{\mathrm{m}}, \chi_A^{\mathrm{m}}, \theta_B^{\mathrm{m}}, \phi_B^{\mathrm{m}}, \chi_B^{\mathrm{m}}). \tag{16-69}$$

We indicate explicitly that the functions $\mu^{(\mathrm{m})}_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A \sigma'_B, \sigma'}$ depend on the inversion coordinates ρ_A and ρ_B.

The symmetry operations (123), (456), (23), and (56) leave the space fixed components of the dipole moment invariant, and they do not change the body fixed (x, y, z) axes. Hence they do not change $\mu_{\mathrm{m}}^{(1,\sigma')}$. This gives rise to conditions analogous to Eqs. (16-61), (16-62), (16-67), and (16-68):

$$\mu^{(\mathrm{m})}_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A \sigma'_B, \sigma'}(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B}) \\ = e^{-ik_A \omega} \mu^{(\mathrm{m})}_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A \sigma'_B, \sigma'}(R, \rho_A, Q'_{r_A}, \rho_B, Q_{r_B}) \tag{16-70}$$

with $Q'_{r_A} = (123) Q_{r_A}$,

$$\mu^{(\mathrm{m})}_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A \sigma'_B, \sigma'}(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B}) \\ = e^{-ik_B \omega} \mu^{(\mathrm{m})}_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A \sigma'_B, \sigma'}(R, \rho_A, Q_{r_A}, \rho_B, Q'_{r_B}) \tag{16-71}$$

with $Q'_{r_B} = (456) Q_{r_B}$,

$$\mu^{(\mathrm{m})}_{\lambda_A \lambda_B \lambda_{AB} -\sigma'_A \sigma'_B, \sigma'}(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B}) \\ = (-1)^{\lambda_A} \mu^{(\mathrm{m})}_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A \sigma'_B, \sigma'}(R, \pi - \rho_A, Q'_{r_A}, \rho_B, Q_{r_B}) \tag{16-72}$$

with $Q'_{r_A} = (23) Q_{r_A}$, and

$$\mu^{(\mathrm{m})}_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A -\sigma'_B, \sigma'}(R, \rho_A, Q_{r_A}, \rho_B, Q_{r_B}) \\ = (-1)^{\lambda_B} \mu^{(\mathrm{m})}_{\lambda_A \lambda_B \lambda_{AB} \sigma'_A \sigma'_B, \sigma'}(R, \rho_A, Q_{r_A}, \pi - \rho_B, Q'_{r_B}) \tag{16-73}$$

with $Q'_{r_{\rm B}} = (56)Q_{r_{\rm B}}$. If we work in the approximation of semirigid moieties, only the $\mu^{\rm (m)}_{\lambda_{\rm A}\lambda_{\rm B}\lambda_{\rm AB}\sigma'_{\rm A}\sigma'_{\rm B},\sigma'}$ with $\sigma'_{\rm A} = 3t_{\rm A}$ and $\sigma'_{\rm B} = 3t_{\rm B}$ would satisfy Eqs. (16-70) and (16-71), but if we allow the moieties to vibrate, nonvanishing functions with other values of $\sigma'_{\rm A}$ and $\sigma'_{\rm B}$ could be constructed by analogy with Eq. (16-64).

The symmetry operation (14)(25)(36)(78) does not affect the space fixed components of the dipole moment, but it reverses the body fixed y and z axes. That is, it leaves μ_x unchanged but reverses the signs of μ_y and μ_z so that Eq. (14-13) yields

$$(14)(25)(36)(78)\,\mu^{(1,\sigma')}_{\rm m} = -\mu^{(1,-\sigma')}_{\rm m}. \tag{16-74}$$

This imposes the following condition:

$$\begin{aligned}&\mu^{\rm (m)}_{\lambda_{\rm B}\lambda_{\rm A}\lambda_{\rm AB}\sigma'_{\rm B}\sigma'_{\rm A},-\sigma'}(R,\rho_{\rm A},Q_{r_{\rm A}},\rho_{\rm B},Q_{r_{\rm B}})\\ &\qquad = (-1)^{\lambda_{\rm A}+\lambda_{\rm B}+1}\,\mu^{\rm (m)}_{\lambda_{\rm A}\lambda_{\rm B}\lambda_{\rm AB}\sigma'_{\rm A}\sigma'_{\rm B},\sigma'}(R,\rho_{\rm B},Q_{r_{\rm B}},\rho_{\rm A},Q_{r_{\rm A}}).\end{aligned} \tag{16-75}$$

The symmetry operation $(23)(56)^*$ reverses the space fixed components of the dipole moment together with the body fixed y and z axes, so that

$$(23)(56)^*\,\mu^{(1,\sigma')}_{\rm m} = \mu^{(1,-\sigma')}_{\rm m}. \tag{16-76}$$

This requires

$$\begin{aligned}&\mu^{\rm (m)}_{\lambda_{\rm A}\lambda_{\rm B}\lambda_{\rm AB}-\sigma'_{\rm A}-\sigma'_{\rm B},-\sigma'}(R,\rho_{\rm A},Q_{r_{\rm A}},\rho_{\rm B},Q_{r_{\rm B}})\\ &\qquad = (-1)^{\lambda_{\rm A}+\lambda_{\rm B}+\lambda_{\rm AB}+\sigma'_{\rm A}+\sigma'_{\rm B}}\mu^{\rm (m)}_{\lambda_{\rm B}\lambda_{\rm A}\lambda_{\rm AB}\sigma'_{\rm B}\sigma'_{\rm A},\sigma'}(R,\rho_{\rm A},Q'_{r_{\rm A}},\rho_{\rm B},Q'_{r_{\rm B}}),\end{aligned} \tag{16-77}$$

with $Q'_{r_{\rm A}} = (23)^*Q_{r_{\rm A}}$ and $Q'_{r_{\rm B}} = (56)^*Q_{r_{\rm B}}$.

We can use Eq. (11-13) to rewrite the basis function of Eq. (16-24) in terms of the $A_{\lambda_{\rm A}\lambda_{\rm B}\lambda_{\rm AB}\sigma'_{\rm A}\sigma'_{\rm B};\sigma'}$ functions

$$\begin{aligned}&\left|n, v^{\rm (A)}_{\rm inv}, v^{\rm (B)}_{\rm inv}, j_{\rm A}, k_{\rm A}, j_{\rm B}, k_{\rm B}, j_{\rm AB}, k; J, m\right\rangle_{\rm (m)}\\ &= (-1)^{j_{\rm A}-j_{\rm B}+k}\,\frac{\sqrt{(2j_{\rm A}+1)(2j_{\rm B}+1)(2j_{\rm AB}+1)}}{8\pi^2}\\ &\times \Phi_{v^{\rm (A)}_{\rm inv},j_{\rm A},k_{\rm A}}(\rho_{\rm A})\,\Phi_{v^{\rm (B)}_{\rm inv},j_{\rm B},k_{\rm B}}(\rho_{\rm B})\,\Phi_n(R,Q_{r_{\rm A}},Q_{r_{\rm B}})\\ &\times A_{j_{\rm A}j_{\rm B}j_{\rm AB}k_{\rm A}k_{\rm B};k}(\theta^{\rm m}_{\rm A},\phi^{\rm m}_{\rm A},\chi^{\rm m}_{\rm A},\theta^{\rm m}_{\rm B},\phi^{\rm m}_{\rm B},\chi^{\rm m}_{\rm B})\,S_{Jkm}(\theta,\phi).\end{aligned} \tag{16-78}$$

We have introduced explicitly in the basis function the inversion functions

$$\Phi_{v^{\rm (M)}_{\rm inv},j_{\rm M},k_{\rm M}}(\rho_{\rm M}) = \left|v^{\rm (M)}_{\rm inv};(j_{\rm M},k_{\rm M})\right\rangle, \tag{16-79}$$

M = A or B, from Eq. (15-40). The transformation properties of the functions in Eq. (16-78) follow directly from the results in Tables 16-8 and 16-9 in conjunction with Eq. (15-41). Taking the function $\Phi_n(R, Q_{r_A}, Q_{r_B})$ to be totally symmetric in the MS group we obtain the transformation properties in Table 16-10. For later use, we have included in the table the transformation properties of the basis functions under the operations $(14)(26)(35)(78)^* = [(23)(56)^*][(14)(25)(36)(78)]$ and $E^* = [(23)][(56)][(23)(56)^*]$, where the square brackets indicate how these operations can be written as products of the chosen generating operations.

Table 16-10

The transformation properties of the functions $\left|n, v_{\rm inv}^{(A)}, v_{\rm inv}^{(B)}, j_A, k_A, j_B, k_B, j_{AB}, k; J, m\right\rangle_{(m)}$ [Eq. (16-78)] in G_{144}.

R	$R\left\lvert v_{\rm inv}^{(A)}, v_{\rm inv}^{(B)}, j_A, k_A, j_B, k_B, k\right\rangle_{(m)}$
(123)	$e^{-ik_A\omega}\left\lvert v_{\rm inv}^{(A)}, v_{\rm inv}^{(B)}, j_A, k_A, j_B, k_B, k\right\rangle_{(m)}$
(456)	$e^{-ik_B\omega}\left\lvert v_{\rm inv}^{(A)}, v_{\rm inv}^{(B)}, j_A, k_A, j_B, k_B, k\right\rangle_{(m)}$
(14)(25)(36)(78)	$(-1)^{J+j_A+j_B}\left\lvert v_{\rm inv}^{(B)}, v_{\rm inv}^{(A)}, j_B, k_B, j_A, k_A, -k\right\rangle_{(m)}$
(23)(56)*	$(-1)^{J+j_A+j_B+j_{AB}+k_A+k_B}\left\lvert v_{\rm inv}^{(A)}, v_{\rm inv}^{(B)}, j_A, -k_A, j_B, -k_B, -k\right\rangle_{(m)}$
(23)	$(-1)^{j_A+v_{\rm inv}^{(A)}}\left\lvert v_{\rm inv}^{(A)}, v_{\rm inv}^{(B)}, j_A, -k_A, j_B, k_B, k\right\rangle_{(m)}$
(56)	$(-1)^{j_B+v_{\rm inv}^{(B)}}\left\lvert v_{\rm inv}^{(A)}, v_{\rm inv}^{(B)}, j_A, k_A, j_B, -k_B, k\right\rangle_{(m)}$
(14)(26)(35)(78)*	$(-1)^{j_{AB}+k_A+k_B}\left\lvert v_{\rm inv}^{(B)}, v_{\rm inv}^{(A)}, j_B, -k_B, j_A, -k_A, k\right\rangle_{(m)}$
E^*	$(-1)^{J+j_{AB}+k_A+k_B+v_{\rm inv}^{(A)}+v_{\rm inv}^{(B)}}\left\lvert v_{\rm inv}^{(A)}, v_{\rm inv}^{(B)}, j_A, k_A, j_B, k_B, -k\right\rangle_{(m)}$

$\omega = 2\pi/3$. We use a shorthand notation for the basis functions, omitting the quantum numbers n, j_{AB}, J, and m which are unaffected by all symmetry operations. The function $\Phi_n(R, Q_{r_A}, Q_{r_B})$ [Eq. (16-78)] is taken to be totally symmetric in G_{144}.

At this point we would like to derive the irreducible representations of G_{144} generated by the basis functions in Eq. (16-78), and to determine the linear combinations that transform irreducibly. In principle, we could do this by using the techniques described in Chapters 5 and 6. We could determine the characters of the operations in G_{144} generated by the basis functions in Eq. (16-78), and reduce the resulting representation by means of Eq. (5-45). Subsequently we could determine symmetrized basis functions by using the projection operators in Eq. (6-64) and the transfer operators in Eq. (6-69), assuming that we have constructed sets of representation matrices associated with the irreducible representations of G_{144}. We are in a position to use these techniques in practice since, with the results in Table 16-10, we could determine the effect of any operation in G_{144} on any basis function. This follows from the fact that all operations in G_{144} can be written as products of the operations contained in Table 16-10. However, it is immediately clear that, owing to the fact that G_{144} has 144 elements, it would be a very tedious task to apply the standard group theoretical methods of Chapters 5 and 6 for this group. Therefore, we use instead the procedure of 'inducing' basis functions symmetrized in G_{144} from basis functions symmetrized in a sequence of subgroups for G_{144}. This is an application of the general idea of decomposing a large group into 'products' of its subgroups which we have briefly mentioned in Section 5.7. The derivation we give here follows in part that of Olthof, van der Avoird, Wormer, Loeser, and Saykally (1994).

We consider first two subgroups of G_{144},

$$\begin{aligned} G^{\mathrm{g}}_{3\mathrm{v}} = \{&E, (123)(456), (132)(465), \\ &(14)(26)(35)(78)^*, (15)(24)(36)(78)^*, (16)(25)(34)(78)^*\} \end{aligned} \tag{16-80}$$

and

$$\begin{aligned} G^{\mathrm{ag}}_{3\mathrm{v}} = \{&E, (123)(465), (132)(456), \\ &(14)(25)(36)(78), (16)(24)(35)(78), (15)(26)(34)(78)\}, \end{aligned} \tag{16-81}$$

where $G^{\mathrm{g}}_{3\mathrm{v}}$ can be said to describe 'geared' rotations of the two moieties, and $G^{\mathrm{ag}}_{3\mathrm{v}}$ 'antigeared' rotations. Both groups are isomorphic to the $C_{3\mathrm{v}}(\mathrm{M})$ group whose character table is given in Table A-6. By analogy with the generating operations (123) and (23)* chosen for $C_{3\mathrm{v}}(\mathrm{M})$ in Section 12.4, we choose the generating operations (123)(456) and

$$I^*_{\mathrm{g}} = (14)(26)(35)(78)^* \tag{16-82}$$

for $G^{\mathrm{g}}_{3\mathrm{v}}$, and (123)(465) and

$$I_{\mathrm{ag}} = (14)(25)(36)(78) \tag{16-83}$$

for $G^{\mathrm{ag}}_{3\mathrm{v}}$.

Table 16-10 shows that

$$\begin{aligned} &(123)(456)\left|n, v^{(\mathrm{A})}_{\mathrm{inv}}, v^{(\mathrm{B})}_{\mathrm{inv}}, j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, k; J, m\right\rangle_{(\mathrm{m})} \\ &\quad = \exp\left(-i\frac{2\pi}{3}g_{\mathrm{g}}\right)\left|n, v^{(\mathrm{A})}_{\mathrm{inv}}, v^{(\mathrm{B})}_{\mathrm{inv}}, j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, k; J, m\right\rangle_{(\mathrm{m})} \end{aligned} \tag{16-84}$$

and

$$\begin{aligned} &(123)(465)\left|n, v^{(\mathrm{A})}_{\mathrm{inv}}, v^{(\mathrm{B})}_{\mathrm{inv}}, j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, k; J, m\right\rangle_{(\mathrm{m})} \\ &\quad = \exp\left(-i\frac{2\pi}{3}g_{\mathrm{ag}}\right)\left|n, v^{(\mathrm{A})}_{\mathrm{inv}}, v^{(\mathrm{B})}_{\mathrm{inv}}, j_{\mathrm{A}}, k_{\mathrm{A}}, j_{\mathrm{B}}, k_{\mathrm{B}}, j_{\mathrm{AB}}, k; J, m\right\rangle_{(\mathrm{m})}, \end{aligned} \tag{16-85}$$

where $g_{\rm g} = k_{\rm A} + k_{\rm B} + 3t_{\rm g}$ and $g_{\rm ag} = k_{\rm A} - k_{\rm B} + 3t_{\rm ag}$. The integers $t_{\rm g}$ and $t_{\rm ag}$ are determined so that $-1 \le g_{\rm g} \le 1$ and $-1 \le g_{\rm ag} \le 1$. The 'quantum numbers' $g_{\rm g}$ and $g_{\rm ag}$ are analogous to the $g_{\rm rv}$ quantum number introduced for symmetric top molecules in Eq. (12-74). The effects of the operations $I_{\rm g}^*$ and $I_{\rm ag}$ on the basis functions are given in Table 16-10.

We use $|g_{\rm g}, g_{\rm ag}\rangle$ as a shorthand notation for the basis function in Eqs. (16-84) and (16-85). It follows from the results of Table 16-10 that if this function has $g_{\rm g} = +1$ (-1), then the function $I_{\rm g}^* |g_{\rm g}, g_{\rm ag}\rangle$ has $g_{\rm g} = -1$ $(+1)$. From Table A-6 it is seen that these two functions transform according to the E irreducible representation of $\boldsymbol{G}_{3\rm v}^{\rm g}$. Otherwise, the two functions $|g_{\rm g}, g_{\rm ag}\rangle$ and $I_{\rm g}^* |g_{\rm g}, g_{\rm ag}\rangle$ both have $g_{\rm g} = 0$ and they transform according to $A_1 + A_2$. In the special case with $k_{\rm A} = k_{\rm B} = 0$ there is only one function, and it transforms according to A_1 *or* A_2. Since $\left(I_{\rm g}^*\right)^2 = E$ we have for functions with $g_{\rm g} = 0$

$$I_{\rm g}^* \left(E \pm I_{\rm g}^*\right) |0, g_{\rm ag}\rangle = \left(I_{\rm g}^* \pm E\right) |0, g_{\rm ag}\rangle = \pm \left(E \pm I_{\rm g}^*\right) |0, g_{\rm ag}\rangle\,, \qquad (16\text{-}86)$$

where the signs in the last expression are correlated. Clearly, $\left(E + I_{\rm g}^*\right) |0, g_{\rm ag}\rangle$ has A_1 symmetry, and $\left(E - I_{\rm g}^*\right) |0, g_{\rm ag}\rangle$ has A_2 symmetry [Table A-6].

The discussion of $\boldsymbol{G}_{3\rm v}^{\rm g}$ in the preceding paragraph can now be repeated for $\boldsymbol{G}_{3\rm v}^{\rm ag}$ with completely analogous results. If the two functions $|g_{\rm g}, g_{\rm ag}\rangle$ and $I_{\rm ag} |g_{\rm g}, g_{\rm ag}\rangle$ have $g_{\rm ag} = \pm 1$, they transform according to the E irreducible representation of $\boldsymbol{G}_{3\rm v}^{\rm ag}$. For functions with $g_{\rm ag} = 0$ we obtain the result that $(E + I_{\rm ag}) |g_{\rm g}, 0\rangle$ has A_1 symmetry, and $(E - I_{\rm ag}) |g_{\rm g}, 0\rangle$ has A_2 symmetry.

At this point, by combining all operations in $\boldsymbol{G}_{3\rm v}^{\rm g}$ with all operations in $\boldsymbol{G}_{3\rm v}^{\rm ag}$, the reader should verify that we obtain the 36 elements in the group $\boldsymbol{G}_{36}$, whose character table is given in Table A-28.[7] If we consider the two moieties of the ammonia dimer to be rigid [i.e., if we consider the barrier between the two equivalent minima of the inversion potential to be insuperable], the MS group of the ammonia dimer would be $\boldsymbol{G}_{36}$. The reader should also notice that $\boldsymbol{G}_{3\rm v}^{\rm g}$ and $\boldsymbol{G}_{3\rm v}^{\rm ag}$ each consist of three whole classes of $\boldsymbol{G}_{36}$ and they are invariant subgroups of $\boldsymbol{G}_{36}$ as defined in Section 5.7. Consequently, $\boldsymbol{G}_{36}$ is the direct product of the two subgroups,

$$\boldsymbol{G}_{36} = \boldsymbol{G}_{3\rm v}^{\rm g} \otimes \boldsymbol{G}_{3\rm v}^{\rm ag}, \qquad (16\text{-}87)$$

where the direct product is discussed in connection with Eq. (1-54) and in Section 5.7. One consequence of $\boldsymbol{G}_{3\rm v}^{\rm g}$ and $\boldsymbol{G}_{3\rm v}^{\rm ag}$ being invariant subgroups of $\boldsymbol{G}_{36}$ is that all elements of $\boldsymbol{G}_{3\rm v}^{\rm g}$ necessarily commute with all elements of $\boldsymbol{G}_{3\rm v}^{\rm ag}$. Another consequence is that the irreducible representations of $\boldsymbol{G}_{36}$ can be labeled as $(\Gamma_{\rm g}, \Gamma_{\rm ag})$, where $\Gamma_{\rm g}$ is an irreducible representation of $\boldsymbol{G}_{3\rm v}^{\rm g}$ and $\Gamma_{\rm ag}$ is an irreducible representation of $\boldsymbol{G}_{3\rm v}^{\rm ag}$ [see Section 5.8.2]. We can obtain a set of basis functions symmetrized in $\boldsymbol{G}_{36}$ by constructing functions that are simultaneously symmetrized in $\boldsymbol{G}_{3\rm v}^{\rm g}$ and $\boldsymbol{G}_{3\rm v}^{\rm ag}$ [see Section 6.3.1]. We have discussed above how to obtain basis functions symmetrized separately in $\boldsymbol{G}_{3\rm v}^{\rm g}$ and

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[7] In Table A-28, $\boldsymbol{G}_{36}$ is defined as the MS group of acetone, but the acetone nuclei are labeled so that the MS group operations are labeled exactly as those used for the ammonia dimer here.

G_{3v}^{ag}, but since all elements of G_{3v}^{g} commute with all elements of G_{3v}^{ag} it is straightforward to derive basis functions symmetrized simultaneously in both groups. The result is given in Table 16-11. Two comments are in order. Even though we could in fact label the irreducible representations of G_{36} as (Γ_g, Γ_{ag}), these representations have the accepted labels used in Table A-28, and these labels are included in Table 16-11 under the heading 'Γ_{36}'. Also, to obtain all the symmetrized basis functions it is sufficient to 'start' from the functions $|g_g, g_{ag}\rangle = |0,0\rangle$, $|1,1\rangle$, $|0,-1\rangle$, and $|-1,0\rangle$, since by applying I_g^* and I_{ag} to these functions, we can generate all other necessary basis functions.

Table 16-11

Basis functions symmetrized in G_{36}.

Γ_{36}	(Γ_g, Γ_{ag})	Partners	Basis function
A_1	(A_1, A_1)		$(E + I_g^*)(E + I_{ag})\|0,0\rangle$
A_2	(A_1, A_2)		$(E + I_g^*)(E - I_{ag})\|0,0\rangle$
A_3	(A_2, A_1)		$(E - I_g^*)(E + I_{ag})\|0,0\rangle$
A_4	(A_2, A_2)		$(E - I_g^*)(E - I_{ag})\|0,0\rangle$
E_1	(A_1, E)	E, I_{ag}	$(E + I_g^*)\|0,-1\rangle$
E_2	(A_2, E)	E, I_{ag}	$(E - I_g^*)\|0,-1\rangle$
E_3	(E, A_1)	E, I_g^*	$(E + I_{ag})\|-1,0\rangle$
E_4	(E, A_2)	E, I_g^*	$(E - I_{ag})\|-1,0\rangle$
G	(E, E)	$E, I_g^*, I_{ag}, I_g^* I_{ag}$	$\|1,1\rangle$

For degenerate irreducible representations of G_{36}, the functions transforming irreducibly are obtained by applying the operations given under the heading 'Partners' to the function given under the heading 'Basis function'. The kets represent the functions $|g_g, g_{ag}\rangle$ (see text). I_g^* and I_{ag} are defined in Eqs. (16-82) and (16-83), respectively.

The next rung on the ladder towards G_{144} is

$$G_{72} = \{G_{36}, G_{36}E^*\} = G_{36} \times \{E, E^*\}, \qquad (16\text{-}88)$$

where we have used the notation for the product of two groups introduced in Eq. (5-61). Equation (16-88) says that G_{72} consists of the 36 elements in G_{36} taken together with the 36 operations obtained by combining each of them with E^*. We can easily verify that E^* commutes with all elements in G_{36}. With this fact as starting point, it is straightforward to show that G_{36} and $\{E, E^*\}$ are both invariant subgroups of G_{72}. Consequently the product in Eq. (16-88) is a direct product:

$$G_{72} = G_{36} \otimes \{E, E^*\}. \qquad (16\text{-}89)$$

The irreducible representations of $\boldsymbol{G}_{72}$ are labeled as $(\Gamma_{36}, \pm)$, where Γ_{36} an irreducible representation of $\boldsymbol{G}_{36}$ and we have used the fact that $\{E, E^*\}$ has the two irreducible representations '+' (for + parity) and '−' (for − parity). Since $\Gamma_{36} = (\Gamma_g, \Gamma_{ag})$, an irreducible representation of $\boldsymbol{G}_{72}$ is labeled as $\Gamma_{72} = (\Gamma_g, \Gamma_{ag}, \pm)$. We let $\Phi^{(\Gamma_g, \Gamma_{ag})}$ denote a basis function from Table 16-11 that transforms according to the irreducible representation (Γ_g, Γ_{ag}) of $\boldsymbol{G}_{36}$. By an argument analogous to that given in Eq. (16-86) [see also Section 6.3.1] we can show that $(E + E^*)\Phi^{(\Gamma_g, \Gamma_{ag})}$ transforms according to the irreducible representation $(\Gamma_g, \Gamma_{ag}, +)$ of $\boldsymbol{G}_{72}$, and $(E - E^*)\Phi^{(\Gamma_g, \Gamma_{ag})}$ transforms according to $(\Gamma_g, \Gamma_{ag}, -)$. The effect of E^* on the basis functions is given in Table 16-10.

Presumably the reader appreciates by now how simple it would be to obtain basis functions symmetrized in $\boldsymbol{G}_{144}$, if $\boldsymbol{G}_{144}$ were a direct product of $\boldsymbol{G}_{72}$ and a group of order 2. Unfortunately we have no such luck. In the notation of Eq. (16-88)

$$\boldsymbol{G}_{144} = \{\boldsymbol{G}_{72}, \boldsymbol{G}_{72}(56)\} = \boldsymbol{G}_{72} \times \{E, (56)\}. \tag{16-90}$$

Inspection of Table A-30 shows that (56) is not in a class of its own[8] in $\boldsymbol{G}_{144}$, so $\{E, (56)\}$ is not an invariant subgroup of this group, and the product in Eq. (16-90) is not a direct product. Since $\boldsymbol{G}_{72}$ *is* an invariant subgroup, the product in Eq. (16-90) is the semidirect product defined in Eq. (5-66):

$$\boldsymbol{G}_{144} = \boldsymbol{G}_{72} \circledS \{E, (56)\}. \tag{16-91}$$

According to Table A-30 the group $\boldsymbol{G}_{144}$ is the direct product $\boldsymbol{G}_{144}^{\mathrm{PSMS}} \otimes \{E, E^*\}$, where $\boldsymbol{G}_{144}^{\mathrm{PSMS}}$ is the permutation subgroup of $\boldsymbol{G}_{144}$. One might think that we should use this decomposition rather than the semidirect product of Eq. (16-91). However this is of little help since the decomposition of $\boldsymbol{G}_{144}^{\mathrm{PSMS}}$ as a product of subgroups also involves a semidirect product. Further, the decomposition given by Eqs. (16-89) and (16-91) has the advantage of directly involving $\boldsymbol{G}_{36}$, the MS group of $(NH_3)_2$ when the moieties are considered rigid. That is, by following the scheme developed here we obtain basis functions symmetrized in both $\boldsymbol{G}_{144}$ and $\boldsymbol{G}_{36}$.

To determine the basis functions symmetrized in $\boldsymbol{G}_{144}$ we use Eq. (16-91) and follow the recipe given in Appendix 16-1 with $\boldsymbol{G} = \boldsymbol{G}_{144}$, $\boldsymbol{H} = \boldsymbol{G}_{72}$, and $S = S^{-1} = (56)$. The recipe requires us to consider the elements of $\boldsymbol{G}_{72}$, R_i with $i = 1, 2, 3, 4, \ldots, 72$, and for each of them to form the transformed element $(56)R_i(56)$. From the transformation matrices $D^{(\Gamma_g, \Gamma_{ag}, \pm)}[R_i]$, $i = 1, 2, 3, 4, \ldots, 72$, chosen for $\boldsymbol{G}_{72}$ [see Appendix 16-2] we must then derive the transformed matrices $D^{(\Gamma_g, \Gamma_{ag}, \pm)}[(56)R_i(56)]$ for each irreducible representation $(\Gamma_g, \Gamma_{ag}, \pm)$ and determine the representation of $\boldsymbol{G}_{72}$ associated with these matrices.

We can facilitate these derivations by labeling the elements of $\boldsymbol{G}_{3v}^{g}$ as $H_j^{(g)}$, $j = 1, 2, 3, 4, 5, 6$, where the sequence of the elements is as given in Eq. (16-80), and those of $\boldsymbol{G}_{3v}^{ag}$ as $H_k^{(ag)}$, $k = 1, 2, 3, 4, 5, 6$, in an analogous manner [see Eq. (16-81)], and by further introducing

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[8] The operation (56) is in the class containing six pair transpositions including (12).

$$\boldsymbol{G}_3^q = \left\{H_1^{(q)}, H_2^{(q)}, H_3^{(q)}\right\} \text{ and } \boldsymbol{K}^q = \left\{H_4^{(q)}, H_5^{(q)}, H_6^{(q)}\right\} \tag{16-92}$$

for 'q' = 'g' or 'ag'. An element[9] $R_i \in \boldsymbol{G}_{72}$ is given by $R_i = H_j^{(g)} H_k^{(ag)}$ or by $R_i = H_j^{(g)} H_k^{(ag)} E^*$, where $H_j^{(g)} H_k^{(ag)} \in \boldsymbol{G}_{36}$. We note that

$$(56) H_j^{(g)} H_k^{(ag)} E^* (56) = \left[(56) H_j^{(g)} H_k^{(ag)} (56)\right] E^* \tag{16-93}$$

since E^* commutes with (56). That is, we can readily transform all elements in $\boldsymbol{G}_{72}$ once we have transformed those in $\boldsymbol{G}_{36}$. The latter transformation produces the results

$$(56) H_j^{(g)} H_k^{(ag)} (56) = H_k^{(g)} H_j^{(ag)} \text{ for } \begin{cases} H_j^{(g)} \in \boldsymbol{G}_3^g \text{ and } H_k^{(ag)} \in \boldsymbol{G}_3^{ag} \\ H_j^{(g)} \in \boldsymbol{K}^g \text{ and } H_k^{(ag)} \in \boldsymbol{K}^{ag} \end{cases} \tag{16-94}$$

and

$$(56) H_j^{(g)} H_k^{(ag)} (56) = H_k^{(g)} H_j^{(ag)} E^* \text{ for } \begin{cases} H_j^{(g)} \in \boldsymbol{G}_3^g \text{ and } H_k^{(ag)} \in \boldsymbol{K}^{ag} \\ H_j^{(g)} \in \boldsymbol{K}^g \text{ and } H_k^{(ag)} \in \boldsymbol{G}_3^{ag}. \end{cases} \tag{16-95}$$

The transformation matrices of $\boldsymbol{G}_{72}$ are chosen as given by Eqs. (16-119) and (16-120) in Appendix 16-2. If we consider first the irreducible representations $(\Gamma_g, \Gamma_{ag}, +)$ [with positive parity] of $\boldsymbol{G}_{72}$, it is clear that the occurrence of the factor E^* in Eq. (16-95) is of no importance since in the construction of representation matrices, E^* will be replaced by its 1×1 representation matrix $+1$ in $\{E, E^*\}$. Thus for these irreducible representations it follows immediately from Eqs. (16-94), (16-95), (16-119), and (16-120) that

$$D^{(\Gamma_g, \Gamma_{ag}, +)}\left[(56) R_i (56)\right] = D^{(\Gamma_{ag}, \Gamma_g, +)}\left[R_i\right]. \tag{16-96}$$

Obviously, the representation of $\boldsymbol{G}_{72}$ associated with the transformed matrices $D^{(\Gamma_g, \Gamma_{ag}, +)}[(56)R_i(56)]$ is $(\Gamma_{ag}, \Gamma_g, +)$. We say that (56) maps $(\Gamma_g, \Gamma_{ag}, +)$ onto $(\Gamma_{ag}, \Gamma_g, +)$ and write

$$(56) : (\Gamma_g, \Gamma_{ag}, +) \rightarrow (\Gamma_{ag}, \Gamma_g, +). \tag{16-97}$$

For the irreducible representations $(\Gamma_g, \Gamma_{ag}, -)$ [with negative parity] the situation is slightly more complicated. In the construction of representation matrices, the factor of E^* in Eq. (16-95) is now replaced by -1, the representation matrix of E^* in $\{E, E^*\}$. However, a few moment's thought shows that

$$(56) : (\Gamma_g, \Gamma_{ag}, -) \rightarrow (A_2 \otimes \Gamma_{ag}, A_2 \otimes \Gamma_g, -). \tag{16-98}$$

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[9] $O \in \boldsymbol{G}$ is a shorthand for saying that the element O is contained in the set $\boldsymbol{G}$.

The irreducible representation A_2 of $\boldsymbol{G}_{3v}^{g}$ or $\boldsymbol{G}_{3v}^{ag}$ has 1 × 1 transformation matrices equal to +1 for the elements in the $\boldsymbol{G}_3^q$ set, and equal to −1 for elements in the $\boldsymbol{K}^q$ set ('q' = 'g' or 'ag'). Multiplication by these matrices produces the required sign change when one of the operations $H_j^{(g)}$ and $H_k^{(ag)}$ belongs to its $\boldsymbol{G}_3^q$ set and the other one to its $\boldsymbol{K}^q$ set, whereas no sign change occurs when both operations are in their respective $\boldsymbol{G}_3^q$ set or in their respective $\boldsymbol{K}^q$ set. We have $A_2 \otimes A_1 = A_2$, $A_2 \otimes A_2 = A_1$, and $A_2 \otimes E = E$.

According to the theory of Appendix 16-1 we distinguish between two cases: In the first case, the l-dimensional irreducible representation $(\Gamma_g, \Gamma_{ag}, \pm)$ of $\boldsymbol{G}_{72}$ is mapped onto itself by (56). We can construct $2l$ basis functions $\boldsymbol{\phi}^{(i)} \pm U(56)\boldsymbol{\phi}^{(i)}$ [where $\boldsymbol{\phi}^{(i)}$ is an l-component column vector containing the basis functions spanning $(\Gamma_g, \Gamma_{ag}, \pm)$ in $\boldsymbol{G}_{72}$, and the $l \times l$ matrix U is defined in Eq. (16-111)] transforming irreducibly according to two l-dimensional irreducible representations of $\boldsymbol{G}_{144}$. In the second case $(\Gamma_g, \Gamma_{ag}, \pm)$ is not mapped onto itself by (56), and $2l$ basis functions, obtained by applying E and (56) to the l basis functions spanning $(\Gamma_g, \Gamma_{ag}, \pm)$ in $\boldsymbol{G}_{72}$, transform according to a $2l$-dimensional irreducible representation of $\boldsymbol{G}_{144}$. It is clear from Eqs. (16-97) and (16-98) that the first case occurs for six irreducible representations of $\boldsymbol{G}_{72}$: $(A_1, A_1, +)$, $(A_2, A_2, +)$, $(A_1, A_2, -)$, $(A_2, A_1, -)$, $(E, E, +)$, and $(E, E, -)$. The first four of these representations are nondegenerate, and each of them gives rise to two nondegenerate irreducible representations of $\boldsymbol{G}_{144}$. The last two representations are fourfold degenerate, and each of them gives rise to two fourfold degenerate representations of $\boldsymbol{G}_{144}$. For all the remaining irreducible representations of G_{72} the second case applies. Thus each of the four nondegenerate representations of $\boldsymbol{G}_{72}$ $(A_1, A_2, +)$, $(A_2, A_1, +)$, $(A_1, A_1, -)$, and $(A_2, A_2, -)$ induces a doubly degenerate irreducible representation of $\boldsymbol{G}_{144}$, and each of the eight doubly degenerate representations of $\boldsymbol{G}_{72}$ $(A_1, E, \pm)$, $(A_2, E, \pm)$, $(E, A_1, \pm)$, and $(E, A_2, \pm)$ induces a fourfold degenerate irreducible representation of $\boldsymbol{G}_{144}$. We have constructed the symmetrized basis functions in such a manner that we know their transformation properties under the operations (123)(456), (123)(465), $I_g^* = (14)(26)(35)(78)^*$, $I_{ag} = (14)(25)(36)(78)$, E^* and, for irreducible representations nondegenerate in $\boldsymbol{G}_{144}$, under (56). With this information, we can identify in Table A-30 the irreducible representation of $\boldsymbol{G}_{144}$ spanned by each set of basis functions.

The results of applying the procedure outlined here are given in Table 16-12. The table gives under the heading 'Γ_{144}' the irreducible representation of $\boldsymbol{G}_{144}$ spanned by the basis functions on the right, and under the heading 'Γ_{72}' it gives the irreducible representation of $\boldsymbol{G}_{72}$ whose associated basis functions induce those spanning Γ_{144}. For the nondegenerate irreducible representations of Γ_{72}, it can easily be recognized in Table 16-12 how the theory is applied. The nondegenerate irreducible representations Γ_{72} that are mapped onto themselves by (56) each give rise to two nondegenerate irreducible representations of $\boldsymbol{G}_{144}$. For nondegenerate irreducible representations the matrix U in Eq. (16-111) is necessarily a one-dimensional unit matrix equal to +1, and the basis functions

Table 16-12

Basis functions symmetrized in G_{144}.

Γ_{144}	Γ_{72}	Partners	Basis function
A_1^+	$(A_1, A_1, +)$	E	$(E+E^*)[E+(56)](E+I_g^*)(E+I_{ag})\|0,0\rangle$
A_1^-	$(A_2, A_1, -)$	E	$(E-E^*)[E+(56)](E-I_g^*)(E+I_{ag})\|0,0\rangle$
A_2^+	$(A_2, A_2, +)$	E	$(E+E^*)[E-(56)](E-I_g^*)(E-I_{ag})\|0,0\rangle$
A_2^-	$(A_1, A_2, -)$	E	$(E-E^*)[E-(56)](E+I_g^*)(E-I_{ag})\|0,0\rangle$
B_1^+	$(A_2, A_2, +)$	E	$(E+E^*)[E+(56)](E-I_g^*)(E-I_{ag})\|0,0\rangle$
B_1^-	$(A_1, A_2, -)$	E	$(E-E^*)[E+(56)](E+I_g^*)(E-I_{ag})\|0,0\rangle$
B_2^+	$(A_1, A_1, +)$	E	$(E+E^*)[E-(56)](E+I_g^*)(E+I_{ag})\|0,0\rangle$
B_2^-	$(A_2, A_1, -)$	E	$(E-E^*)[E-(56)](E-I_g^*)(E+I_{ag})\|0,0\rangle$
E^+	$(A_1, A_2, +)$	E, (56)	$(E+E^*)(E+I_g^*)(E-I_{ag})\|0,0\rangle$
E^+	$(A_2, A_1, +)$	(56), E	$(E+E^*)(E-I_g^*)(E+I_{ag})\|0,0\rangle$
E^-	$(A_1, A_1, -)$	E, (56)	$(E-E^*)(E+I_g^*)(E+I_{ag})\|0,0\rangle$
E^-	$(A_2, A_2, -)$	(56), E	$(E-E^*)(E-I_g^*)(E-I_{ag})\|0,0\rangle$
G_1^+	$(E, E, +)$	E, I_{ag}, $I_{ag}(23)$, (23)	$(E+E^*)[E+(56)]\|1,1\rangle$
G_1^-	$(E, E, -)$	E, I_{ag}, $-I_{ag}(23)$, $-(23)$	$(E-E^*)[E+(56)]\|1,1\rangle$
G_2^+	$(E, E, +)$	E, I_{ag}, $-I_{ag}(23)$, $-(23)$	$(E+E^*)[E-(56)]\|1,1\rangle$
G_2^-	$(E, E, -)$	E, I_{ag}, $I_{ag}(23)$, (23)	$(E-E^*)[E-(56)]\|1,1\rangle$
G_3^+	$(A_2, E, +)$	E, $-(23)(56)$, (56), $-(23)$	$(E+E^*)(E-I_g^*)\|0,-1\rangle$
G_3^+	$(E, A_2, +)$	(56), (23), E, $-(23)(56)$	$(E+E^*)(E-I_{ag})\|-1,0\rangle$
G_3^-	$(A_1, E, -)$	E, $-(23)(56)$, (56), $-(23)$	$(E-E^*)(E+I_g^*)\|0,-1\rangle$
G_3^-	$(E, A_2, -)$	(56), $-(23)$, E, (23)(56)	$(E-E^*)(E-I_{ag})\|-1,0\rangle$
G_4^+	$(A_1, E, +)$	E, (23)(56), (56), (23)	$(E+E^*)(E+I_g^*)\|0,-1\rangle$
G_4^+	$(E, A_1, +)$	(56), (23), E, (23)(56)	$(E+E^*)(E+I_{ag})\|-1,0\rangle$
G_4^-	$(A_2, E, -)$	E, (23)(56), (56), (23)	$(E-E^*)(E-I_g^*)\|0,-1\rangle$
G_4^-	$(E, A_1, -)$	(56), $-(23)$, E, $-(23)(56)$	$(E-E^*)(E+I_{ag})\|-1,0\rangle$

For degenerate irreducible representations of G_{144}, the functions transforming irreducibly are obtained by applying the operations given under the heading 'Partners' to the function given under the heading 'Basis function'. The kets represent the functions $|\theta_g, \theta_{ag}\rangle$ (see text). All function sets belonging to the same representation generate identical representation matrices. The character tables for the groups G_{36} and G_{144} are given in Tables A-28 and A-30, respectively. $I_g^* = (14)(26)(35)(78)^*$ and $I_{ag} = (14)(25)(36)(78)$.

symmetrized in G_{144} are obtained by applying $E\pm(56)$ to those symmetrized in G_{72}. The nondegenerate irreducible representations Γ_{72} that are not mapped onto themselves by (56) each give rise to a doubly degenerate irreducible representation (E^+ or E^-) of $\boldsymbol{G}_{144}$, and the basis functions symmetrized in $\boldsymbol{G}_{144}$ are obtained by applying E and (56) to those symmetrized in $\boldsymbol{G}_{72}$. The derivation of the basis functions spanning the fourfold degenerate irreducible representations $G_i^{\pm}$, $i = 1, 2, 3, 4$, in $\boldsymbol{G}_{144}$ is less transparent. There are two reasons for this. The irreducible representations $G_1^{\pm}$ and $G_2^{\pm}$ are induced by the fourfold irreducible representations $(E, E, \pm)$ of $\boldsymbol{G}_{72}$. The $(E, E, \pm)$ representations are mapped onto themselves by (56), but the U matrix involved [Eq. (16-111)] is not a unit matrix. This complicates the expression $\boldsymbol{\phi}^{(i)} \pm U\,(56)\boldsymbol{\phi}^{(i)}$ for the basis functions symmetrized in $\boldsymbol{G}_{144}$. The remaining irreducible representations of $\boldsymbol{G}_{144}$, $G_3^{\pm}$ and $G_4^{\pm}$, are induced by doubly degenerate irreducible representations of $\boldsymbol{G}_{72}$. In principle, the basis functions symmetrized in $\boldsymbol{G}_{144}$ could be obtained by applying E and (56) to those symmetrized in $\boldsymbol{G}_{72}$. However, $G_3^{\pm}$ and $G_4^{\pm}$ each appear twice in Table 16-12, spanned by different basis functions. It is desirable that each set of basis functions spanning a given degenerate irreducible representation of $\boldsymbol{G}_{144}$ generate the same representation matrices. With the basis functions chosen in this way, the Hamiltonian matrix block for an l-dimensional irreducible representation will split into l sub-blocks, where each sub-block has the same eigenvalues.[10] The basis functions for the $E^{\pm}$, $G_3^{\pm}$, and $G_4^{\pm}$ irreducible representations in Table 16-12 are chosen so that all function sets belonging to the same representation generate identical representation matrices. We refer the reader to the publication by Olthof, van der Avoird, Wormer, Loeser, and Saykally (1994) for the details of the derivation.

We derive the spin statistical weights for $(^{14}NH_3)_2$ by using Eq. (8-28) to determine the characters of the representation $\Gamma^{\rm sw}_{\rm rve}$ of $\boldsymbol{G}_{144}$ (see Section 8.4.1) and reducing this representation. The result is

$$\begin{aligned}\Gamma^{\rm sw}_{\rm rve} &= 78\,A_2{}^+ \oplus 66\,B_2{}^+ \oplus 72\,G_2{}^+ \oplus 21\,G_3{}^+ \oplus 15\,G_4{}^+\\ &\oplus 78\,A_2{}^- \oplus 66\,B_2{}^- \oplus 72\,G_2{}^- \oplus 21\,G_3{}^- \oplus 15\,G_4{}^-. \qquad (16\text{-}99)\end{aligned}$$

Levels of symmetry $A_1{}^{\pm}$, $B_1{}^{\pm}$, $E^{\pm}$, and $G_1{}^{\pm}$ are missing.

We mentioned above that if, on the time scale of the experiment being interpreted, the barrier between the two equivalent inversion minima of the two ammonia moieties is insuperable, then the MS group of the ammonia dimer would be $\boldsymbol{G}_{36}$. In Table 16-13, we give the correlation table, and the reverse correlation table (see Section 5.9), for the two groups $\boldsymbol{G}_{144}$ and $\boldsymbol{G}_{36}$. The reverse correlation table has the spin statistical weights from Eq. (16-99) added. It shows that the inversion motion of the ammonia moieties causes no splittings (but shifts) of levels nondegenerate in $\boldsymbol{G}_{36}$. Levels doubly degenerate in $\boldsymbol{G}_{36}$ split into two levels, each fourfold degenerate in $\boldsymbol{G}_{144}$, and levels fourfold degenerate in $\boldsymbol{G}_{36}$ also split into two levels, each fourfold degenerate in $\boldsymbol{G}_{144}$.

In $\boldsymbol{G}_{144}$, the electric dipole representation $\Gamma^* = A_1{}^-$. The rigorous selection rules obtained from Eq. (14-8) are

$$\Gamma^+ \leftrightarrow \Gamma^- \qquad (16\text{-}100)$$

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[10] See Footnote 7 on page 120.

Table 16-13

Correlation and reverse correlation tables for the G_{144} and G_{36} groups of the ammonia dimer

G_{144}	G_{36}	G_{144}	G_{36}	G_{36}	G_{144}
$A_1{}^+$	A_1	$A_1{}^-$	A_3	A_1	$A_1{}^+(0) \oplus B_2{}^+(66) \oplus E^-(0)$
$A_2{}^+$	A_4	$A_2{}^-$	A_2	A_2	$A_2{}^-(78) \oplus B_1{}^-(0) \oplus E^+(0)$
$B_1{}^+$	A_4	$B_1{}^-$	A_2	A_3	$A_1{}^-(0) \oplus B_2{}^-(66) \oplus E^+(0)$
$B_2{}^+$	A_1	$B_2{}^-$	A_3	A_4	$A_2{}^+(78) \oplus B_1{}^+(0) \oplus E^-(0)$
E^+	$A_2 \oplus A_3$	E^-	$A_1 \oplus A_4$	E_1	$G_4{}^+(15) \oplus G_3{}^-(21)$
$G_1{}^+$	G	$G_1{}^-$	G	E_2	$G_3{}^+(21) \oplus G_4{}^-(15)$
$G_2{}^+$	G	$G_2{}^-$	G	E_3	$G_4{}^+(15) \oplus G_4{}^-(15)$
$G_3{}^+$	$E_2 \oplus E_4$	$G_3{}^-$	$E_1 \oplus E_4$	E_4	$G_3{}^+(21) \oplus G_3{}^-(21)$
$G_4{}^+$	$E_1 \oplus E_3$	$G_4{}^-$	$E_2 \oplus E_3$	G	$G_1{}^+(0) \oplus G_2{}^+(72)$ $\oplus G_1{}^-(0) \oplus G_2{}^-(72)$

In the reverse correlation table (Section 5.9), the spin statistical weights are added (see Section 8.5). The character tables for the groups G_{36} and G_{144} are given in Tables A-28 and A-30, respectively.

where, in practice, $\Gamma = A_2, B_2, G_2, G_3$, and G_4, since levels of other symmetries are missing. In order for the matrix element given in Eq. (16-27) of $\mu_s^{(1,\sigma)}$ between the basis functions in Eq. (16-24) to be nonvanishing, we have the usual triangular[11] condition $\Delta(J''J'1)$ together with $\Delta(j''_A j'_A \lambda_A)$, $\Delta(j''_B j'_B \lambda_B)$, and $\Delta(j''_{AB} j'_{AB} \lambda_{AB})$. Further, we have the condition $\sigma' = k' - k'' = \Delta k$, which we also obtained for the individual terms in Eq. (14-33), together with $\sigma'_A = k'_A - k''_A = \Delta k_A$ and $\sigma'_B = k'_B - k''_B = \Delta k_B$. We discussed in connection with Eqs. (16-70) and (16-71) the fact that in the approximation of rigid moieties, only terms with $\sigma'_A = 3t_A$ and $\sigma'_B = 3t_B$ (where t_A and t_B are integers) will occur in the expression for the dipole moment. In this case we have $\Delta k_A = 3t_A$ and $\Delta k_B = 3t_B$. For transitions with $\Delta k_M = 3t_M \pm 1$, M = A or B, to acquire nonvanishing intensities we must allow for the intra-moiety vibrational motions; such transitions will be caused by terms in the expansion of the dipole moment depending on the normal coordinates of the moieties, for example as indicated by Eq. (16-64). The transitions are necessarily accompanied by a change in v_t, the harmonic oscillator quantum number associated with the normal coordinates $Q_t{}^{(M)\pm}$ [see Eq. (16-64) and Chapter 14], and so they are vibrational transitions of the moieties.

In Fig. 16-6 we show a $(^{14}NH_3)_2$ transition originally observed by Nelson, Fraser, and Klemperer (1985) but recorded here by Prof. W. Stahl at much higher resolution. Both states involved in this transition have G symmetry in G_{36}. From Table 16-13 we see that a level of G symmetry in G_{36} splits into two

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[11] See Footnote 1 on page 563.

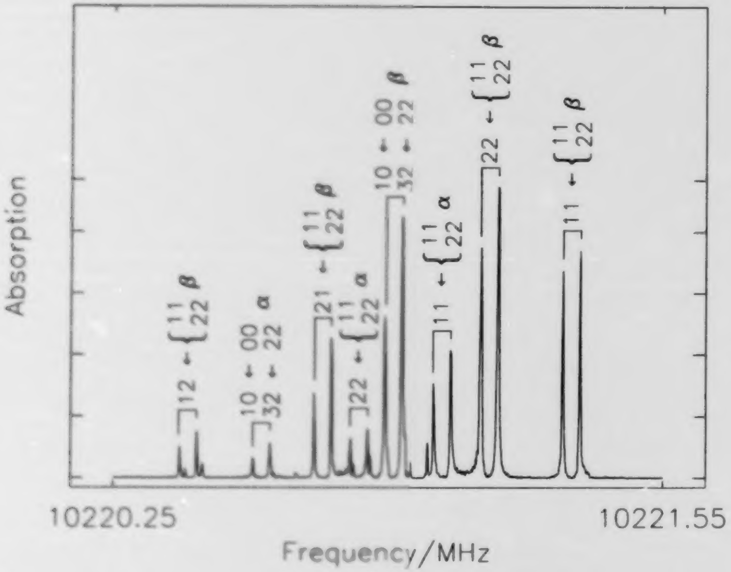

Fig. 16-6. The $(J,K) = (1,0) \leftarrow (0,0)$ transition of $(^{14}NH_3)_2$ involving the two lowest states of G symmetry in G_{36} [see Fig. 2 of van Bladel, van der Avoird, Wormer, and Saykally (1992)]. This spectrum was taken by Prof. W. Stahl with a pulsed molecular beam Fourier transform microwave spectrometer [see Heineking, Stahl, Olthof, Wormer, van der Avoird, and Havenith (1995) and references therein]. In this experimental technique, each transition of the molecule gives rise to a doublet in the spectrum, the two components being split by twice the Doppler shift caused by the velocity of the molecules in the molecular beam. Here, this splitting is approximately 40.3 kHz corresponding to a speed of 591 m/s for the ammonia dimers. The doublets are indicated in the figure and labeled by $F'I' \leftarrow F''I''$, where F is the total angular momentum quantum number and I is obtained by coupling the spins of the two nitrogen nuclei [see Sections 13.6.2 and 14.1.6], and by α or β which label the tunneling state (see text). The weak unassigned Doppler doublet that almost overlaps the high frequency shoulder of the $12 \leftarrow (11,22)$ β doublet is the $21 \leftarrow (11,22)$ α doublet. In the spectrum shown here every line is due to two unresolved $F'I' \leftarrow F''I''$ transitions.

levels with G_{144} symmetries G_2^+ and G_2^-, respectively, when moiety inversion is taken into account. The $G \leftarrow G$ transition splits into two allowed transitions, $G_2^- \leftarrow G_2^+$ and $G_2^+ \leftarrow G_2^-$ [Eq. (16-100)] which we label α and β. Each of them is further split into hyperfine components due to the quadrupole coupling of the two ^{14}N nuclei, and the combined effect of the two sources of splitting produces the pattern in Fig. 16-6.

APPENDIX 16-1: SEMIDIRECT PRODUCTS

We consider a group $\boldsymbol{G}$ that can be written as the semidirect product [see Eq. (5-66)] of two subgroups, an invariant subgroup $\boldsymbol{H}$ of order h and a (non-invariant) subgroup $\{E, S\}$ of order 2,

$$\boldsymbol{G} = \boldsymbol{H} \circledS \{E, S\}. \tag{16-101}$$

The group $\boldsymbol{H}$ has the elements

$$\boldsymbol{H} = \{H_1, H_2, H_3, \ldots, H_h\}. \tag{16-102}$$

We denote by $\Phi_1^{(i)}$, $\Phi_2^{(i)}$, $\Phi_3^{(i)}$, ..., $\Phi_{l_i}^{(i)}$ a set of basis functions that transform according to the irreducible representation Γ_i of $\boldsymbol{H}$, and which generate the representation matrices $D^{(i)}[H_k]$:

$$H_k \, \Phi_m^{(i)} = \sum_{n=1}^{l_i} D^{(i)}[H_k]_{mn} \Phi_n^{(i)}. \tag{16-103}$$

If $\{E, S\}$ were an invariant subgroup of $\boldsymbol{G}$, so that $\boldsymbol{G}$ were a direct product, then we could construct the functions $(E \pm S)\,\Phi_m^{(i)}$ which would transform according to the irreducible representation $(\Gamma_i, \pm)$ of $\boldsymbol{G}$. This is the way we used the direct product $\boldsymbol{G}_{72} = \boldsymbol{G}_{36} \otimes \{E, E^*\}$ in Section 16.5.2. In the present case of a semidirect product it is more complicated to construct basis functions that transform irreducibly in $\boldsymbol{G}$ from those that transform irreducibly in $\boldsymbol{H}$.

We must investigate how the functions $\Phi_m^{(i)}$ transform in the group $\boldsymbol{G}$ with the elements

$$\boldsymbol{G} = \{H_1, H_2, H_3, \ldots, H_h, H_1S, H_2S, H_3S, \ldots, H_hS\}. \tag{16-104}$$

The transformation properties under an operation H_k is given by Eq. (16-103), and we can derive the transformation properties under H_kS by using the fact that $\boldsymbol{H}$ is an invariant subgroup of $\boldsymbol{G}$. Because of this, we have $S^{-1}H_kS = H_{k'} \in \boldsymbol{H}$, or $H_kS = SH_{k'}$. Thus, from Eq. (16-103)

$$H_k \, S \, \Phi_m^{(i)} = S \, H_{k'} \, \Phi_m^{(i)} = \sum_{n=1}^{l_i} D^{(i)}[H_{k'}]_{mn} \, S \, \Phi_n^{(i)}. \tag{16-105}$$

We consider the set of $2l_i$ functions $\Phi_1^{(i)}$, $\Phi_2^{(i)}$, $\Phi_3^{(i)}$, ..., $\Phi_{l_i}^{(i)}$, $S\Phi_1^{(i)}$, $S\Phi_2^{(i)}$, $S\Phi_3^{(i)}$, ..., $S\Phi_{l_i}^{(i)}$ and wish to determine their symmetry in $\boldsymbol{G}$. The transformation properties of all of these functions under any of the operations in $\boldsymbol{G}$ can be obtained from Eqs. (16-103) and (16-105) as we now show. The effect of an element H_k of $\boldsymbol{G}$ acting on a function $\Phi_m^{(i)}$ is given by Eq. (16-103), and the effect of this operation acting on $S\Phi_m^{(i)}$ is given by Eq. (16-105). The effect of an element H_kS acting on $\Phi_m^{(i)}$ is given by Eq. (16-105), and the effect of

$H_k S$ acting on $S\Phi_m^{(i)}$ is given by Eq. (16-103) since, because $\{E, S\}$ is a group of order 2 and therefore by necessity $S^2 = E$,

$$H_k S\left(S\,\Phi_m^{(i)}\right) = H_k\,\Phi_m^{(i)}. \tag{16-106}$$

With the $2l_i$-element column vector

$$\boldsymbol{\Phi}^{(i)} = \begin{bmatrix} \boldsymbol{\phi}^{(i)} \\ S\boldsymbol{\phi}^{(i)} \end{bmatrix}, \tag{16-107}$$

where $\boldsymbol{\phi}^{(i)}$ is an l_i-element column vector

$$\boldsymbol{\phi}^{(i)} = \begin{bmatrix} \Phi_1^{(i)} \\ \Phi_2^{(i)} \\ \vdots \\ \Phi_{l_i}^{(i)} \end{bmatrix}, \tag{16-108}$$

the $2l_i \times 2l_i$ transformation matrix generated by an operation H_k in $\boldsymbol{G}$ is defined by

$$H_k\boldsymbol{\Phi}^{(i)} = \begin{bmatrix} D^{(i)}[H_k] & 0 \\ 0 & D^{(i)}[S^{-1}H_kS] \end{bmatrix}\boldsymbol{\Phi}^{(i)}, \tag{16-109}$$

where each element in this apparent 2×2 matrix represents an $l_i \times l_i$ block (and '0' is such a block of zeroes). Similarly, the transformation matrix generated by an operation H_kS in $\boldsymbol{G}$ is defined by

$$H_kS\boldsymbol{\Phi}^{(i)} = \begin{bmatrix} 0 & D^{(i)}[S^{-1}H_kS] \\ D^{(i)}[H_k] & 0 \end{bmatrix}\boldsymbol{\Phi}^{(i)}. \tag{16-110}$$

In practical applications, we could determine the characters of the transformation matrices in Eqs. (16-109) and (16-110) and use Eq. (5-45) to reduce the representation associated with them in terms of the irreducible representations of $\boldsymbol{G}$. However, it can be formally proved that there are only two possibilities for the result of this reduction. The first case occurs if there exists a unitary matrix U so that

$$D^{(i)}[S^{-1}H_kS] = U^{-1}\,D^{(i)}[H_k]\,U \text{ for all } H_k \in \boldsymbol{H}. \tag{16-111}$$

The simplest situation arises if the matrix U is the $l_i \times l_i$ unit matrix, i.e., if $D^{(i)}[S^{-1}H_kS] = D^{(i)}[H_k]$ for all $H_k \in \boldsymbol{H}$. In this case we obtain basis functions symmetrized in $\boldsymbol{G}$ by applying the operators $(E \pm S)$ to the basis functions symmetrized in $\boldsymbol{H}$, just as in the case of a direct product. If $D^{(i)}[S^{-1}H_kS] = D^{(i)}[H_k]$ for all H_k, we determine the effect of H_k on the vector $(E \pm S)\,\boldsymbol{\phi}^{(i)}$ using

$$\begin{aligned} H_k\,(E \pm S)\,\boldsymbol{\phi}^{(i)} &= D^{(i)}[H_k]\,\boldsymbol{\phi}^{(i)} \pm D^{(i)}[S^{-1}H_kS]\,S\,\boldsymbol{\phi}^{(i)} \\ &= D^{(i)}[H_k]\,(E \pm S)\,\boldsymbol{\phi}^{(i)} \end{aligned} \tag{16-112}$$

and the effect of H_kS using

$$
\begin{aligned}
H_kS\,(E \pm S)\,\phi^{(i)} &= \pm H_k\,(E \pm S)\,\phi^{(i)} \\
&= \pm D^{(i)}[H_k]\,(E \pm S)\,\phi^{(i)}
\end{aligned}
\tag{16-113}
$$

since $S\,(E \pm S) = \pm(E \pm S)$. Equations (16-112) and (16-113) show that the basis function sets $(E + S)\,\phi^{(i)}$ and $(E - S)\,\phi^{(i)}$ transform according to two different l_i-dimensional irreducible representations of $\boldsymbol{G}$. These representations cannot be reduced further since if this were possible, the irreducible representation Γ_i of $\boldsymbol{H}$ could also be reduced. If U exists but is not a unit matrix [so that the matrices $D^{(i)}[S^{-1}H_kS]$ and $D^{(i)}[H_k]$ are equivalent but not identical], it can be shown that the two sets of basis functions $\phi^{(i)} \pm U\,S\phi^{(i)}$ transform according to two different l_i-dimensional irreducible representations of $\boldsymbol{G}$.

If the matrices $D^{(i)}[S^{-1}H_kS]$ and $D^{(i)}[H_k]$ are non-equivalent so that no U matrix can be found to fulfill Eq. (16-111), the $2l_i$ basis functions in the vector $\boldsymbol{\Phi}^{(i)}$ transform according to a $2l_i$-dimensional irreducible representation of $\boldsymbol{G}$. We omit the formal proofs of this result and of the results obtained when U exists but is not a unit matrix. The reader should refer to Section II.6 of Jansen and Boon (1967), which describes the general relationships between the irreducible representations and the symmetrized basis functions of a group and its subgroups.

In practice, we distinguish between the situations described above by considering the matrices $D^{(i)}[S^{-1}H_kS]$, $k = 1, 2, 3, \ldots, h$. Since the matrices $D^{(i)}[H_1]$, $D^{(i)}[H_2]$, $D^{(i)}[H_3]$, $\ldots$, $D^{(i)}[H_h]$ form a representation of $\boldsymbol{H}$ and $S^{-1}H_jSS^{-1}H_kS = S^{-1}H_jH_kS$, it is easy to show that the matrices $D^{(i)}[S^{-1}H_kS]$, $k = 1, 2, 3, \ldots, h$, also form a representation of $\boldsymbol{H}$. If this representation is Γ_i [in which case we say that Γ_i is *mapped onto itself* by S], there exists a U matrix to satisfy Eq. (16-111), and the basis functions in $\boldsymbol{\Phi}^{(i)}$ transform according to two l_i-dimensional irreducible representations of $\boldsymbol{G}$. If the representation is not Γ_i no U matrix exists, and the basis functions in $\boldsymbol{\Phi}^{(i)}$ transform according to a $2l_i$-dimensional irreducible representation of $\boldsymbol{G}$.

APPENDIX 16-2: REPRESENTATION MATRICES OF G_{72}

In Section 16.5.2 we consider the group $\boldsymbol{G}_{72}$ which is the direct product of the groups $\boldsymbol{G}^{\mathrm{g}}_{3\mathrm{v}}$, $\boldsymbol{G}^{\mathrm{ag}}_{3\mathrm{v}}$, and $\{E, E^*\}$ according to Eqs. (16-87) and (16-89). An irreducible representation of $\boldsymbol{G}_{72}$ is labeled as $\Gamma_{72} = (\Gamma_{\mathrm{g}}, \Gamma_{\mathrm{ag}}, \pm)$, where Γ_{g}, Γ_{ag}, and $\pm$ are irreducible representations of $\boldsymbol{G}^{\mathrm{g}}_{3\mathrm{v}}$, $\boldsymbol{G}^{\mathrm{ag}}_{3\mathrm{v}}$, and $\{E, E^*\}$, respectively. Consequently, basis functions symmetrized in $\boldsymbol{G}_{72}$ can be chosen to be symmetrized simultaneously in $\boldsymbol{G}^{\mathrm{g}}_{3\mathrm{v}}$, $\boldsymbol{G}^{\mathrm{ag}}_{3\mathrm{v}}$, and $\{E, E^*\}$. We denote such a basis function as $\Phi^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}_{m_{\mathrm{g}},m_{\mathrm{ag}}}$. If the operation $H_j^{(\mathrm{g})} \in \boldsymbol{G}^{\mathrm{g}}_{3\mathrm{v}}$ and $H_k^{(\mathrm{ag})} \in \boldsymbol{G}^{\mathrm{ag}}_{3\mathrm{v}}$ we can write

$$
H_j^{(\mathrm{g})}\,\Phi^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}_{m_{\mathrm{g}},m_{\mathrm{ag}}} = \sum_{m'_{\mathrm{g}}=1}^{l_{\mathrm{g}}} D^{(\Gamma_{\mathrm{g}})}\left[H_j^{(\mathrm{g})}\right]_{m_{\mathrm{g}}m'_{\mathrm{g}}}\,\Phi^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}_{m'_{\mathrm{g}},m_{\mathrm{ag}}}
\tag{16-114}
$$

and

$$H_k^{(\mathrm{ag})}\,\Phi_{m_{\mathrm{g}},m_{\mathrm{ag}}}^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)} = \sum_{m'_{\mathrm{ag}}=1}^{l_{\mathrm{ag}}} D^{(\Gamma_{\mathrm{ag}})}\left[H_k^{(\mathrm{ag})}\right]_{m_{\mathrm{ag}}m'_{\mathrm{ag}}} \Phi_{m_{\mathrm{g}},m'_{\mathrm{ag}}}^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}, \tag{16-115}$$

where l_{g} and l_{ag} are the dimensions of Γ_{g} and Γ_{ag}, respectively, together with

$$E^*\,\Phi_{m_{\mathrm{g}},m_{\mathrm{ag}}}^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)} = (\pm 1)\,\Phi_{m_{\mathrm{g}},m_{\mathrm{ag}}}^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}. \tag{16-116}$$

The two groups $\boldsymbol{G}_{3\mathrm{v}}^{\mathrm{g}}$ and $\boldsymbol{G}_{3\mathrm{v}}^{\mathrm{ag}}$ are isomorphic. Consequently, we can choose the basis functions so that they generate the same transformation matrices $D^{(\Gamma)}$ in these two groups. The symmetrized basis functions in Table 16-11 are chosen in this manner. If $\Gamma_{\mathrm{g}} = \Gamma_{\mathrm{ag}}$ and $H_j^{(\mathrm{g})}$ and $H_j^{(\mathrm{ag})}$ are partner operations, connected by the isomorphism, in $\boldsymbol{G}_{3\mathrm{v}}^{\mathrm{g}}$ and $\boldsymbol{G}_{3\mathrm{v}}^{\mathrm{ag}}$, respectively, we have for the representation matrices

$$D^{(\Gamma_{\mathrm{g}})}\left[H_j^{(\mathrm{g})}\right] = D^{(\Gamma_{\mathrm{ag}})}\left[H_j^{(\mathrm{ag})}\right]. \tag{16-117}$$

The representation matrices $D^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}[R]$ generated by the basis functions $\Phi_{m_{\mathrm{g}},m_{\mathrm{ag}}}^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}$ in $\boldsymbol{G}_{72}$ are formally defined by

$$R\,\Phi_{m_{\mathrm{g}},m_{\mathrm{ag}}}^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)} = \sum_{m'_{\mathrm{g}},m'_{\mathrm{ag}}} D^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}[R]_{m_{\mathrm{g}}m_{\mathrm{ag}},m'_{\mathrm{g}}m'_{\mathrm{ag}}}\,\Phi_{m'_{\mathrm{g}},m'_{\mathrm{ag}}}^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}, \tag{16-118}$$

where $R \in \boldsymbol{G}_{72}$. We have $R = H_j^{(\mathrm{g})}\,H_k^{(\mathrm{ag})}$ or $R = H_j^{(\mathrm{g})}\,H_k^{(\mathrm{ag})}\,E^*$. Comparison of Eq. (16-118) with Eqs. (16-114)-(16-116) shows

$$\begin{aligned} &D^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}\left[H_j^{(\mathrm{g})}\,H_k^{(\mathrm{ag})}\right]_{m_{\mathrm{g}}m_{\mathrm{ag}},m'_{\mathrm{g}}m'_{\mathrm{ag}}} \\ &\qquad = D^{(\Gamma_{\mathrm{g}})}\left[H_j^{(\mathrm{g})}\right]_{m_{\mathrm{g}}m'_{\mathrm{g}}} D^{(\Gamma_{\mathrm{ag}})}\left[H_k^{(\mathrm{ag})}\right]_{m_{\mathrm{ag}}m'_{\mathrm{ag}}} \end{aligned} \tag{16-119}$$

and

$$\begin{aligned} &D^{(\Gamma_{\mathrm{g}},\Gamma_{\mathrm{ag}},\pm)}\left[H_j^{(\mathrm{g})}\,H_k^{(\mathrm{ag})}\,E^*\right]_{m_{\mathrm{g}}m_{\mathrm{ag}},m'_{\mathrm{g}}m'_{\mathrm{ag}}} \\ &\qquad = (\pm 1)\,D^{(\Gamma_{\mathrm{g}})}\left[H_j^{(\mathrm{g})}\right]_{m_{\mathrm{g}}m'_{\mathrm{g}}} D^{(\Gamma_{\mathrm{ag}})}\left[H_k^{(\mathrm{ag})}\right]_{m_{\mathrm{ag}}m'_{\mathrm{ag}}}. \end{aligned} \tag{16-120}$$

BIBLIOGRAPHICAL NOTES

Review articles

Hutson (1990,1991). These reviews give a systematic introduction to the theory of the dynamics of weakly bound clusters, and to the study of their use in determining intermolecular forces.

Chemical Reviews (1994). This issue of Chemical Reviews contains 15 papers that cover dynamics and *ab initio* theoretical studies, as well as a wide range of experimental works.

Faraday Discussions (1994). This report contains the 24 papers, and the discussions, presented at the General Discussion of the Faraday Society held at the University of Durham U.K. on 6–8 April 1994 on "The Structure and Dynamics of van der Waals Molecules."

Nesbitt (1994). This paper reviews experimental infrared absorption laser spectroscopic studies of weakly bound cluster molecules produced by cooling in a pulsed adiabatic expansion through a slit. Experimental and theoretical studies of the clusters Ar_nHF and Ar_nDF for $n = 1, 2, 3$ and 4 are reported. Studies of $(DF)_3$ are also discussed.

Wales (1996). This paper reviews the different approaches that can be used to study the potential energy surfaces of weakly bound cluster molecules.

Liu, Cruzan and Saykally (1996). This paper briefly reviews progress in theoretical and experimental studies of water clusters from the trimer to the hexamer

Bačić and Miller (1996). This paper reviews the way the intermolecular potential is determined, and the way the dynamics are understood, for dimers (all without writing a single equation).

Bačić (1997). This paper reviews studies of the infrared spectrum and structure of Ar_nHF clusters for $n = 1$ to 14.

The ammonia dimer

Odutola, Dyke, Howard, and Muenter (1979). The electric deflection behavior of a molecular beam of mass selected ammonia dimers [together with $(NH_3)_3$, $(NH_3)_4$, $(NH_3)_5$, and $(NH_3)_6$ clusters] is studied. The dimer is found to be polar, and the higher polymers nonpolar, from which it is concluded that the dimer probably has a single linear (or nearly linear) N-H-N hydrogen-bond. It is pointed out that, since the dimer is polar, a study of its microwave spectrum would be possible, although very complicated to interpret. The MS group G_{144} is introduced. Unfortunately some of the spin statistical weights given in this paper are incorrect; they are corrected in Havenith, Linnartz, Zwart, Kips, ter Meulen, and Meerts (1992). Eq. (16-99) here has the correct values.

Nelson, Fraser, and Klemperer (1985). A key paper in the study of the nature of the hydrogen bond. Microwave spectra are reported for $(^{14}NH_3)_2$ and several isotopomers. The experimentally determined values of the rotational constants are found to be inconsistent with a 'classical' linear or nearly linear hydrogen bond.

Sagarik, Ahlrichs, and Brode (1986). An *ab initio* study in which it is shown that electron correlation effects have a crucial influence on the equilibrium geometry. At the SCF level the equilibrium structure has a linear hydrogen bond, but after including electron correlation effects the equilibrium structure is obtained as the cyclic C_{2h} structure of Fig. 16-5. However, the calculated potential energy changes by only a small amount as the structure distorts away from the C_{2h} structure in the manner shown in Fig. 16-5; in contrast, the calculated dipole moment increases very quickly.

Nelson, Klemperer, Fraser, Lovas, and Suenram (1987). Further rotational spectra are measured for $(^{14}NH_3)_2$ and several isotopomers. The spectra confirm that the structure deviates strongly from one with a linear hydrogen-bond.

Havenith, Linnartz, Zwart, Kips, ter Meulen, and Meerts (1992). This is an infrared–far-infrared double resonance experiment performed on $(NH_3)_2$ molecules in a jet, and splittings in the spectrum caused by inversion of the ammonia moieties are identified. The feasibility of the donor-acceptor interchange (depicted here in Fig.16-5) and of the internal rotation of the moieties are also included in the analysis, and the G_{144} group is used. Upon excitation of the ν_2 umbrella mode the inversion splitting is found to be 3.7 cm^{-1}.

Loeser, Schmuttenmaer, Cohen, Elrod, Steyert, Saykally, Bumgarner, and Blake (1992). This paper reports more than 800 far-infrared absorption lines and 12 new microwave absorption lines of the ammonia dimer; it also comes to the conclusion that moiety inversion, donor-acceptor interchange and torsional tunneling motions are all significant, and the G_{144} group is used in the analysis. In $K = 0$ states inversion splittings of from 1.1 to 3.3 GHz are measured, while in two $K=1$ states splittings of 48 and 9 MHz are measured. It is pointed out that, as a result of the fact that the molecule is so nonrigid, the structures reported by

Nelson, Fraser, and Klemperer (1985) and by Nelson, Klemperer, Fraser, Lovas, and Suenram (1987) are not equilibrium structures, but structures resulting from averaging over the large-amplitude vibrational motion.

van Bladel, van der Avoird, Wormer and Saykally (1992). This paper reports the first six-dimensional calculation of the ammonia dimer bound levels, and it uses the *ab initio* potential of Sagarik, Ahlrichs, and Brode (1986). It is shown that vibrational averaging, especially over the donor-acceptor interchange path, strongly affects the dipole moment and nuclear quadrupole splittings used to determine the geometry. It is concluded that the $G_\alpha - G_\beta$ doublets found by Nelson, Fraser, and Klemperer (1985) correspond to a single intermolecular vibrational state that is split by ammonia inversion tunneling.

Linnartz, Kips, Meerts, and Havenith (1993). Stark splittings (see Section 14.5) are measured for a band of $(NH_3)_2$ at 486.8 GHz using a supersonic jet expansion; the dipole moment is determined for the $|k| = 1$ state with G symmetry in G_{36}. The transitions are of the type $G_2^+ \leftrightarrow G_2^-$ and G_{144} is used in the analysis. A symmetry analysis of the Stark splittings is given. The small value of the dipole moment obtained (0.1 D) supports the idea of an essentially C_{2h} vibrationally averaged structure. A linear hydrogen bonded structure would have a dipole moment of about 2 D.

Tao and Klemperer (1993). A large basis set *ab initio* MP2 study is performed and bond functions are incorporated into the basis set. The equilibrium structure of $(NH_3)_2$ is obtained as the cyclic C_{2h} structure but with only a gradual rise in the potential as the molecule distorts away from this structure in the directions indicated in Fig. 16-5. It is pointed out that the (weak) dependence of the intermoiety potential on the angular orientations of the moieties over a range of angles near that of the C_{2h} geometry is critically determined by the dispersion forces. Apart from this work, and the work of Sagarik, Ahlrichs, and Brode (1986), we do not quote the results of other *ab initio* studies on the ammonia dimer; they generally find the equilibrium structure to be the linear hydrogen bonded structure.

van der Avoird, Wormer, and Moszynski (1994). A review article, summarizing the results obtained for $(NH_3)_2$ up to 1994.

Olthof, van der Avoird, and Wormer (1994). A model potential energy surface for the intermolecular motion of $(NH_3)_2$ is set up, and it is used in six-dimensional calculations of bound levels. This reproduces satisfactorily the experimental results of Loeser, Schmuttenmaer, Cohen, Elrod, Steyert, Saykally, Bumgarner, and Blake (1992). The equilibrium geometry is found to be as that depicted in Fig. 16-4, but the barrier at the C_{2h} configuration (see Fig. 16-5) is determined to be only 7 cm^{-1}. Bound states of $(ND_3)_2$ are also calculated, and it is shown why deuteration has only a small effect on the dipole moment (reducing it) and on the nuclear quadrupole splittings even though there is facile large amplitude donor-acceptor tunneling [Nelson, Fraser, and Klemperer (1985) erroneously conclude from these observed small isotope effects that a relatively rigid near-C_{2h} structure obtains]. As mentioned at the end of Section 15.4.1 an NH_3 molecule can be in either an ortho or para nuclear spin state; in $(NH_3)_2$, states of A symmetry in G_{36} are ortho-ortho, states of E symmetry are para-para and states of G symmetry are ortho-para. In this paper it is shown that the different internal rotor behavior of ortho and para NH_3 and ND_3 is important.

Olthof, van der Avoird, Wormer, Loeser, and Saykally (1994). This paper gives the derivation of basis functions for $(NH_3)_2$ symmetrized in G_{144}. The basis functions derived are essentially those of Table 16-12. It should be noted, however, that in this paper the basis functions for the inversion motion of the moieties are sums and differences of the functions given in Eq. (16-79) here. Also in their Table V, the kets represent the functions $|k_\mathrm{A}, k_\mathrm{B}\rangle$, and not the functions $|g_\mathrm{g}, g_\mathrm{ag}\rangle$ that we use here. The theory is used to calculate the splitting patterns in the spectra of $(NH_3)_2$, and quantitative agreement is obtained with the experimental results of Loeser, Schmuttenmaer, Cohen, Elrod, Steyert, Saykally, Bumgarner, and Blake (1992).

Heineking, Stahl, Olthof, Wormer, van der Avoird, and Havenith (1995). Nuclear quadrupole splittings for $(NH_3)_2$, calculated from wavefunctions based on the potential energy surface of Olthof, van der Avoird, and Wormer (1994), are compared with experimental results and a good agreement is obtained.

Cotti, Linnartz, Meerts, van der Avoird, and Olthof (1996). Stark splittings (see Section 14.5) are measured for a band at 747.2 GHz, and the results analyzed theoretically using

G_{144}. The dipole moment varies very significantly with rotation-contortional state, and there is a strong K dependence. The results confirm the highly nonrigid nature of the ammonia dimer. Because of the low rigidity of this molecule the rotation-contortional wavefunctions have significant probability distribution over a wide range of contortional coordinates. The dipole moment is strongly dependent on the values of the coordinates [see, for example, Sagarik, Ahlrichs, and Brode (1986)] and hence small changes in the coordinate probability distribution cause significant changes in the value of the dipole moment. To understand the effect of the intermolecular interaction, measurements of dipole moment values, as well as of energies, are clearly important.

17

Linear Molecules

The application of permutation-inversion symmetry, and the methods used for the calculation of rovibronic energies, are discussed for linear molecules. The treatment of MS group symmetry, and the use of a harmonic oscillator-rigid rotor basis in the calculation of rotation-vibration energies, have to be modified. We derive the rovibronic Hamiltonian for a diatomic molecule, the simplest linear molecule, and determine the transformation properties of the associated rovibronic coordinates under permutation-inversion operations. For a general polyatomic linear molecule we introduce Hougen's isomorphic Hamiltonian which is much more convenient to work with than the true Hamiltonian. The form of the eigenfunctions of the isomorphic Hamiltonian, and their classification in the molecular point group, and in the MS group, are discussed. It is shown that the MS group cannot be used to classify the vibronic eigenfunctions. The extended MS group of a linear molecule is introduced, and this group, like the MS group of a nonlinear rigid molecule, is isomorphic to the molecular point group and can be used to classify both vibronic and rovibronic eigenfunctions. We explain both the e/f and c/d notations used for labeling the rotational energy levels of linear molecules, as well as the correlation between the energy levels (and quantum number labels) of linear and bent triatomic molecules. At the end of the chapter we discuss g/u interaction in the diatomic molecules H_2^+ and I_2.

17.1 INTRODUCTION

In Chapter 10, we discuss the coordinates used in the rotation-vibration Schrödinger equation for a nonlinear rigid molecule. The rotational coordinates are the three Euler angles (θ, ϕ, χ) [see Fig. 10-1], and to determine their values, for a particular nuclear geometry, we solve three transcendental equations obtained from the three Eckart equations given in Eqs. (10-27)-(10-29). These equations involve the values of the molecule fixed coordinates of the nuclei at the equilibrium configuration given by (x_i^e, y_i^e, z_i^e), where $i = 1, 2, 3, \ldots, N$. For a linear molecule it is customary to choose the molecule fixed axis system so that at equilibrium all nuclei are on the z axis. That is $(x_i^e, y_i^e, z_i^e) = (0, 0, z_i^e)$. In this situation, one of the Eckart equations [Eq. (10-27)] is always satisfied, and the two other equations [Eqs. (10-28) and (10-29)] reduce to

$$\sum_{i=1}^{N} m_i z_i^{e} y_i = 0 \tag{17-1}$$

and

$$\sum_{i=1}^{N} m_i z_i^{e} x_i = 0. \tag{17-2}$$

These two equations enable us to determine θ and ϕ, and thus the spatial orientation of the z axis, from the instantaneous coordinates of the nuclei in space; there is no Eckart condition that specifies the Euler angle χ.

It is obvious that the treatment of molecular rotation and vibration outlined in Chapters 10 and 11 cannot be applied to a linear molecule without modification. For a nonlinear molecule, we make a zero-order treatment of rotation and vibration by solving the zero-order rotational Schrödinger equation [Eq. (11-6); this equation involves the three rotational coordinates (θ, ϕ, χ)] and the $3N-6$ independent zero-order vibrational Schrödinger equations [Eq. (11-7); each of these equations involves one normal coordinate Q_r]. We cannot treat a linear molecule in the same way since the rotational coordinate χ is not defined.

Among linear molecules, diatomic molecules are special in that they are always linear, regardless of the value of their one (stretching) vibrational coordinate. The two nuclei cannot possibly rotate around the z axis, and thus diatomic molecules have two rotational degrees of freedom (described by the Euler angles θ and ϕ which define the instantaneous direction of the molecular axis) and one vibrational degree of freedom (described by the internuclear distance R). We discuss diatomic molecules in Section 17.3.

For polyatomic molecules the situation is different, and a particular polyatomic chain molecule will have the same number of rotational and vibrational degrees of freedom, regardless of whether its equilibrium structures is linear or nonlinear. If the equilibrium structure is nonlinear, we can treat it using the zero-order model discussed in Chapters 10 and 11, although this will not be very successful if the barrier to linearity is low compared to the bending energy separations. If the equilibrium structure is linear, the treatment breaks down completely because the Eckart equations do not define χ. However, the molecule *can* rotate around the z axis, the problem is just that in order to do so, it must first bend out of the linear equilibrium configuration. Our zero-order treatment fails because we insist on separating the rotation around the z axis from the vibrational motion; this is not permissible for a linear molecule. There are two ways around the problem. The first way is to use a zero-order treatment in which we separate the Schrödinger equation into one for both the rotation and the bending degrees of freedom, and another for the other vibrations. This is done (at least for triatomic molecules) in the HBJ approach [Hougen, Bunker, and Johns (1970)] summarized in Chapter 15 and applied to CH_2 in Section 15.4.7. The second way is to separate the Schrödinger equation into one involving only the two rotational degrees of freedom described by θ and ϕ, and another for all the vibrations and the rotation around the z axis. This latter zero order separation is used in the "standard" theory for the rotation-vibration motion of a linear molecule.

In the next section we discuss the relation between the HBJ and standard treatments of rotation-bending motion in linear triatomic molecules. After that we concentrate on explaining the standard rotation-vibration theory for linear molecules. We first give a detailed discussion of the diatomic molecule in order to show, for a relatively simple example, the problems that arise when the equilibrium configuration is linear, and then we show how these problems are solved by using the isomorphic Hamiltonian.

17.2 LINEAR TRIATOMIC MOLECULES

In the HBJ approach, the three rotational degrees of freedom and the bending vibration of a triatomic molecule are described by the Hamiltonian $\hat{H}_{rc}$ in Eq. (15-5). The terms associated with the bending motion and the rotation around the z axis are given in the Hamiltonian $\hat{H}_{\mathrm{con},z}$ in Eq. (15-98). We will now apply $\hat{H}_{\mathrm{con},z}$ to a *linear* triatomic molecule. In zero order we consider the bending vibration to be harmonic; thus the bending potential function $V_0(\rho)$ in Eq. (15-98) is

$$V_0(\rho) = \frac{1}{2} k_\rho \rho^2. \tag{17-3}$$

The coordinate ρ is defined as the supplement of the bond angle of the triatomic molecule in the reference configuration [see Chapter 15], and the molecule is linear for $\rho = 0$. We have already mentioned in Chapter 15 that the ρ-dependent function $\mu_{\rho\rho}^{\mathrm{ref}}$ in Eq. (15-98) varies slowly with ρ. When the bending potential function is given by Eq. (17-3) with k_ρ large, the molecule will carry out small oscillations around the linear configuration, ρ will always be small, and we can approximate the function $\mu_{\rho\rho}^{\mathrm{ref}}$ by $\mu_{\rho\rho}^{\mathrm{ref}}(0)$, its value at linearity ($\rho = 0$). In this approximation, the second term on the right hand side of Eq. (15-98) vanishes and the second and third terms can be approximated by means of Eqs. (15-97) and (15-94), respectively. Thus, in the Hougen-Bunker-Johns approach we obtain the following zero order Hamiltonian for the bending and z-axis rotation of a linear triatomic molecule:

$$\hat{H}_{\mathrm{lin}} = \frac{\mu_{\rho\rho}^{\mathrm{ref}}(0)}{2} \left\{ -\hbar^2 \frac{\partial^2}{\partial \rho^2} - \frac{\hbar^2}{4\rho^2} + \frac{1}{\rho^2} \hat{J}_z^2 \right\} + \frac{1}{2} k_\rho \rho^2. \tag{17-4}$$

With the definitions $Q = \rho/\sqrt{\mu_{\rho\rho}^{\mathrm{ref}}(0)}$, $\lambda = k_\rho \mu_{\rho\rho}^{\mathrm{ref}}(0)$, and $\hat{J}_z = -i\hbar\partial/\partial\chi$ we can simplify Eq. (17-4) to

$$\hat{H}_{\mathrm{lin}} = \frac{1}{2} \left[-\hbar^2 \left(\frac{\partial^2}{\partial Q^2} + \frac{1}{4Q^2} + \frac{1}{Q^2} \frac{\partial^2}{\partial \chi^2} \right) + \lambda Q^2 \right]. \tag{17-5}$$

The zero order rotation-bending wavefunctions and energies of the linear triatomic molecule [i.e., the eigenfunctions of $\hat{H}_{\mathrm{rc}}$ in Eq. (15-5)] can be obtained as described, for example, in Section 6 of Jensen (1983a).

In the standard theory the bending vibration and the rotation around the z axis for a triatomic molecule are treated together as a two-dimensional isotropic harmonic oscillator [see Chapter 11]. This will be discussed in detail for the HCN molecule below. The Hamiltonian for these motions, analogous to $\hat{H}_{\mathrm{lin}}$ above, is $\hat{H}_{\mathrm{tdho}}$ given by Eq. (11-150) which we repeat here:

$$\hat{H}_{\mathrm{tdho}} = \frac{1}{2}\left[-\hbar^2\left(\frac{\partial^2}{\partial Q^2} + \frac{1}{Q}\frac{\partial}{\partial Q} + \frac{1}{Q^2}\frac{\partial^2}{\partial \chi^2}\right) + \lambda Q^2\right]. \qquad (17\text{-}6)$$

We have made the change of notation $\alpha \rightarrow \chi$ relative to Eq. (11-150). For a triatomic molecule, the angle α introduced for the two-dimensional harmonic oscillator is equal to the Euler angle χ employed in the HBJ approach. The angular momentum quantum number k employed in the HBJ approach is called l in the two-dimensional isotropic harmonic oscillator. We see that even though we have expressed $\hat{H}_{\mathrm{lin}}$ and $\hat{H}_{\mathrm{tdho}}$ in terms of the same coordinates Q and χ, these two Hamiltonians are not identical as we would perhaps initially expect.

The reason for the difference between $\hat{H}_{\mathrm{lin}}$ and $\hat{H}_{\mathrm{tdho}}$ is purely technical. We have obtained $\hat{H}_{\mathrm{lin}}$ from the operator $\hat{H}_{\mathrm{con},z}$ in Eq. (15-98); the operator $\hat{H}_{\mathrm{con},z}$ is consistent with the volume element $d\rho\, d\chi$. It then follows from the discussion in connection with Eq. (9-30) that $\hat{H}_{\mathrm{lin}}$ is consistent with the volume element $dQ\, d\chi$ [since Q is proportional to ρ; in this case the weight factor s in Eq. (9-30) is a constant and does not change the form of the Hamiltonian]. On the other hand the Hamiltonian $\hat{H}_{\mathrm{tdho}}$ is consistent with a volume element of $dQ_a\, dQ_b = Q\, dQ\, d\chi$ [see Eq. (5-7) in Margenau and Murphy (1956) together with Eqs. (11-146) and (11-147)]. Thus, if we follow the ideas discussed in connection with Eq. (9-30) and set $s = Q$, we obtain

$$\hat{H}_{\mathrm{tdho}} = Q^{-1/2}\hat{H}_{\mathrm{lin}}Q^{1/2}. \qquad (17\text{-}7)$$

It is left as an exercise to the reader to verify this relation [see also Boháček, Papoušek, Pick, and Špirko (1976)].

We have shown that the HBJ and standard approaches lead to the same description for the harmonic bending and z axis rotation for a linear triatomic molecule; the apparent difference between the Hamiltonians $\hat{H}_{\mathrm{lin}}$ and $\hat{H}_{\mathrm{tdho}}$ is due entirely to different choices of the volume element used for the normalization of the wavefunction. These different choices, however, have important implications for the detailed form of the eigenfunctions of the two Hamiltonians. The eigenfunctions of $\hat{H}_{\mathrm{tdho}}$ are the $\Psi_{v,l}$ functions given by Eq. (11-166):

$$\hat{H}_{\mathrm{tdho}}\, \Psi_{v,l} = E_v\, \Psi_{v,l}, \qquad (17\text{-}8)$$

where E_v is given by Eq. (11-167). By inserting Eq. (17-7) in this equation, we obtain

$$\hat{H}_{\mathrm{lin}}\left(Q^{1/2}\,\Psi_{v,l}\right) = E_v\left(Q^{1/2}\,\Psi_{v,l}\right). \qquad (17\text{-}9)$$

That is, the eigenfunctions $\Psi_{v,l}^{(\mathrm{lin})}$ of $\hat{H}_{\mathrm{lin}}$ are given as

$$\Psi_{v,l}^{(\mathrm{lin})} = Q^{1/2}\Psi_{v,l}. \tag{17-10}$$

For example, the wavefunction $\Psi_{0,0}$, describing the vibrational ground state of the linear triatomic molecule in the $\hat{H}_{\mathrm{tdho}}$ picture, is given by Eq. (11-165). It is a Gaussian function of Q which attains it maximum value at $Q = 0$, i.e., at the linear configuration. In the $\hat{H}_{\mathrm{lin}}$ picture from the HBJ approach, this function is replaced by

$$\Psi_{0,0}^{(\mathrm{lin})} = (\gamma/\pi)^{1/2}Q^{1/2}\exp[-(\gamma Q^2/2)] \tag{17-11}$$

[with $\gamma = \sqrt{\lambda}/\hbar$, see Eq. (11-106)], which attains its *minimum* value of zero at $Q = 0$. The behavior of $\Psi_{0,0}^{(\mathrm{lin})}$ for Q near 0 is in accordance with Eq. (15-105) since Q is proportional to ρ and $k = l = 0$ here. The difference between eigenfunctions of $\hat{H}_{\mathrm{lin}}$ and $\hat{H}_{\mathrm{tdho}}$ expressed in Eq. (17-10) has often been a source of considerable confusion when descriptions of the linear molecule based on the HBJ approach have been compared with descriptions based on a two-dimensional isotropic harmonic oscillator. However, as we have shown here, the two descriptions are equivalent and the difference in the form of the wavefunction is a simple consequence of different choices for the volume element.

In the standard theory based on one- and two-dimensional isotropic harmonic oscillators, we describe a general, N-atomic linear molecule as having two rotational degrees of freedom and $3N - 5$ vibrational degrees of freedom, described by $3N - 5$ normal coordinates Q_r. Of these $3N - 5$ coordinates, $N - 1$ correspond to one-dimensional harmonic oscillators and describe the stretching vibrations, and there are $N - 2$ coordinate pairs (Q_{ta}, Q_{tb}) corresponding to two-dimensional isotropic harmonic oscillators and describing the bending vibrations [see, for example, Papoušek and Aliev (1982)]. For a diatomic molecule, the $3 \times 2 - 5 = 1$ vibrational degree of freedom is a "true" vibration [in that it causes the relative positions of the nuclei to change]; it is the stretching of the internuclear distance. For a polyatomic linear molecule, however, one of the $3N - 5 \geq 4$ vibrational degrees of freedom is really the rotation around the z axis and is not a vibration. There will be some combination of the $3N - 5$ vibrational coordinates which, for nonlinear geometries, describes the molecule rotating around the z axis with the relative positions of the nuclei remaining unchanged. For the reasons given above, this motion is treated together with the true vibrations in the standard approach.

17.3 DIATOMIC MOLECULES

17.3.1 Changing to rovibronic coordinates

For a diatomic molecule, in which the nuclei are labeled 1 and 2 and the n electrons $3, 4, \ldots, n+2$, the molecule fixed (x, y, z) axis system is fixed so that the z axis points from nucleus 1 to nucleus 2. This defines the two rotational variables θ and ϕ; we choose $\chi = 0°$ in order to define the location of the x and y axes. The Euler angle χ is arbitrary since there are only two rotational degrees of freedom for the nuclei in a diatomic molecule. The nuclei and axis system are drawn in Fig. 17-1 where nucleus 1 is assumed heavier than nucleus 2. We change coordinates in the wave equation from $(\xi_2, \eta_2, \zeta_2, \ldots, \zeta_{n+2})$ to $(\theta, \phi, R, x_3, y_3, z_3, \ldots, z_{n+2})$, where R is the internuclear distance. This coordinate change is made in the hope of separating the rotational (θ, ϕ), vibrational (R), and electronic (x_i, y_i, z_i) variables in the resultant wave equation, and we use Method I for this coordinate change.

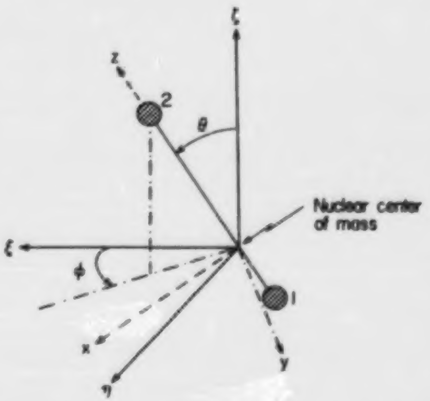

Fig. 17-1. The (x, y, z) axis system for a diatomic molecule where z is defined as pointing from nucleus 1 to nucleus 2, and χ is chosen as zero.

From Fig. 17-1 and Eqs. (10-5) and (10-7) we see that the two sets of coordinates are related by

$$\theta = \arccos[\zeta_2(\xi_2^2 + \eta_2^2 + \zeta_2^2)^{-1/2}], \tag{17-12}$$

$$\phi = \arccos[\xi_2(\xi_2^2 + \eta_2^2)^{-1/2}] = \arcsin[\eta_2(\xi_2^2 + \eta_2^2)^{-1/2}], \tag{17-13}$$

$$R = [(m_1 + m_2)/m_1](\xi_2^2 + \eta_2^2 + \zeta_2^2)^{1/2}, \tag{17-14}$$

$$x_i = \xi_i \cos\theta \cos\phi + \eta_i \cos\theta \sin\phi - \zeta_i \sin\theta, \tag{17-15}$$

$$y_i = -\xi_i \sin\phi + \eta_i \cos\phi, \tag{17-16}$$

and

$$z_i = \xi_i \sin\theta \cos\phi + \eta_i \sin\theta \sin\phi + \zeta_i \cos\theta, \tag{17-17}$$

where $i = 3, 4, \ldots, n+2$, and the restriction $0 \le \theta \le \pi$ holds. It is important to notice that we can calculate the Euler angles θ and ϕ directly from the nuclear coordinates (ξ_2, η_2, ζ_2) using Eqs. (17-12) and (17-13). Following the Method I coordinate change through for the nuclear kinetic energy operator $\hat{T}_N$ involves a lengthy but straightforward use of the chain rule and we obtain intermediate results such as

$$\frac{\partial}{\partial \xi_2} = \frac{m_1 + m_2}{m_1 R \sin\theta} \left\{ \sum_{k=3}^{n+2} \left[-\cos\theta(\sin\phi y_k + \sin\theta\cos\phi z_k)\frac{\partial}{\partial x_k} \right.\right.$$
$$\left. + \sin\phi(\cos\theta x_k + \sin\theta z_k)\frac{\partial}{\partial y_k} + \sin\theta(\cos\theta\cos\phi x_k - \sin\phi y_k)\frac{\partial}{\partial z_k} \right]$$
$$\left. + \cos\phi\cos\theta\sin\theta\frac{\partial}{\partial\theta} - \sin\phi\frac{\partial}{\partial\phi} + R\cos\phi\sin^2\theta\frac{\partial}{\partial R} \right\} \tag{17-18}$$
$$= \frac{m_1 + m_2}{m_1 R\sin\theta}\left[-i\sin\theta\sin\phi\left(\frac{\hat{L}_x}{\hbar}\right) - i\cos\theta\sin\theta\cos\phi\left(\frac{\hat{L}_y}{\hbar}\right) \right.$$
$$+ i\cos\theta\sin\phi\left(\frac{\hat{L}_z}{\hbar}\right) + \cos\phi\cos\theta\sin\theta\frac{\partial}{\partial\theta}$$
$$\left. - \sin\phi\frac{\partial}{\partial\phi} + R\cos\phi\sin^2\theta\frac{\partial}{\partial R}\right], \tag{17-19}$$

where the electronic angular momentum operators are defined by

$$\hat{L}_x = -i\hbar\sum_{k=3}^{n+2}\left(y_k\frac{\partial}{\partial z_k} - z_k\frac{\partial}{\partial y_k}\right), \tag{17-20}$$

and cyclically for $\hat{L}_y$ and $\hat{L}_z$. From Eq. (9-50) we deduce that for a diatomic molecule

$$\hat{T}_N = -\frac{\hbar^2}{2m_2}\nabla_2^2 + \frac{\hbar^2}{2(m_1+m_2)}\nabla_2^2$$
$$= -\frac{\hbar^2 m_1}{2m_2(m_1+m_2)}\nabla_2^2. \tag{17-21}$$

Changing coordinates using the chain rule [see Eq. (17-19)] gives

$$\hat{T}_N = -\frac{\hbar^2}{2\mu}\nabla^2_{R\theta\phi}, \tag{17-22}$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{17-23}$$

and

$$\nabla^2_{R\theta\phi} = \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{1}{R^2\sin^2\theta}\left[\frac{\partial}{\partial\phi} + i\frac{\hat{L}_x}{\hbar}\sin\theta - i\frac{\hat{L}_z}{\hbar}\cos\theta\right]^2$$
$$+ \frac{1}{R^2\sin\theta}\left[\frac{\partial}{\partial\theta} - i\frac{\hat{L}_y}{\hbar}\right]\sin\theta\left[\frac{\partial}{\partial\theta} - i\frac{\hat{L}_y}{\hbar}\right]. \tag{17-24}$$

The electronic angular momentum has crept into the nuclear kinetic energy operator, and it is instructive to introduce (x, y, z) components of the rovibronic angular momentum operator in place of the operators $\partial/\partial\theta$ and $\partial/\partial\phi$. The rovibronic angular momentum operator[1] $\hat{\boldsymbol{J}}$ has components in the (ξ, η, ζ) axis system given by

$$\hat{J}_\xi = -i\hbar \sum_{j=1}^{n+2} \left(\eta_j \frac{\partial}{\partial \zeta_j} - \zeta_j \frac{\partial}{\partial \eta_j} \right) \tag{17-25}$$

and cyclically for $\hat{J}_\eta$ and $\hat{J}_\zeta$. As shown in Eq. (10-90) these three operators do not commute with each other and we have

$$[\hat{J}_\xi, \hat{J}_\eta] = \hat{J}_\xi \hat{J}_\eta - \hat{J}_\eta \hat{J}_\xi = i\hbar \hat{J}_\zeta \tag{17-26}$$

with two similar commutators obtained by cyclically permuting $\hat{J}_\xi$, $\hat{J}_\eta$, and $\hat{J}_\zeta$. Using equations such as Eq. (17-19), the inverses of Eqs. (17-12)–(17-17), and the direction cosine matrix with $\chi = 0°$ to obtain $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ from $\hat{J}_\xi$, $\hat{J}_\eta$, and $\hat{J}_\zeta$, we find that

$$\hat{J}_x = i\hbar \csc\theta \frac{\partial}{\partial\phi} + \cot\theta \hat{L}_z, \tag{17-27}$$

$$\hat{J}_y = -i\hbar \frac{\partial}{\partial\theta}, \tag{17-28}$$

and

$$\hat{J}_z = \hat{L}_z. \tag{17-29}$$

Substituting these equations into Eq. (17-24) we can write Eq. (17-22) as

$$\begin{aligned} \hat{T}_{\mathrm{N}} = -\frac{1}{2\mu R^2}\Bigg[& \hbar^2 \frac{\partial}{\partial R}\left(R^2 \frac{\partial}{\partial R}\right) - (\hat{J}_x - \hat{L}_x)^2 \\ & - \frac{1}{\sin\theta}(\hat{J}_y - \hat{L}_y)\sin\theta(\hat{J}_y - \hat{L}_y)\Bigg], \end{aligned} \tag{17-30}$$

where the terms in $\hat{J}_x\hat{L}_x$ and $\hat{J}_y\hat{L}_y$ are those that give rise to the Coriolis coupling effects on the electrons. The following commutators are important and can be easily derived:

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[1] $\hat{\boldsymbol{J}}$ is used here for the rovibronic angular momentum operator instead of the more correct $\hat{\boldsymbol{N}}$ [see the footnote on page 138]. This is in order to follow accepted usage in the rovibronic Hamiltonian. For a singlet electronic state $\hat{\boldsymbol{J}} = \hat{\boldsymbol{N}}$.

$$[\hat{J}_x, \hat{J}_y] = -i\hbar\cot\theta\,\hat{J}_x - i\hbar\hat{L}_z, \tag{17-31}$$

$$[\hat{J}_y, \hat{J}_z] = [\hat{J}_z, \hat{J}_x] = 0, \tag{17-32}$$

$$[\hat{J}_x, \hat{L}_\beta] = i\hbar\cot\theta\sum_\gamma \varepsilon_{z\beta\gamma}\hat{L}_\gamma, \tag{17-33}$$

$$[\hat{J}_y, \hat{L}_\beta] = 0, \tag{17-34}$$

$$[\hat{J}_z, \hat{L}_\beta] = i\hbar\sum_\gamma \varepsilon_{z\beta\gamma}\hat{L}_\gamma, \tag{17-35}$$

and

$$[\hat{L}_\alpha, \hat{L}_\beta] = i\hbar\sum_\gamma \varepsilon_{\alpha\beta\gamma}\hat{L}_\gamma, \tag{17-36}$$

where α, β, $\gamma = x$, y, or z, and $\varepsilon_{\alpha\beta\gamma}$ is given by Eq. (10-91).

As a result of this coordinate change we can write the rovibronic Schrödinger equation of a diatomic molecule as

$$\begin{aligned}[][\hat{T}_e + \hat{T}_{\text{vib}} + \hat{T}_{\text{rot}} + V(R, x_3, y_3, z_3, \ldots, z_{n+2})\\ - E_{\text{rve}}]\Phi_{\text{rve}}(R, \theta, \phi, x_3, \ldots, z_{n+2}) = 0,\end{aligned} \tag{17-37}$$

where

$$\hat{T}_e = -\frac{\hbar^2}{2m_e}\sum_{i=3}^{n+2}\nabla_i^2 - \frac{\hbar^2}{2M_N}\sum_{i,j=3}^{n+2}\nabla_i\cdot\nabla_j, \tag{17-38}$$

$$\hat{T}_{\text{vib}} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right), \tag{17-39}$$

and

$$\hat{T}_{\text{rot}} = \frac{1}{2\mu R^2}\left[(\hat{J}_x - \hat{L}_x)^2 + \frac{1}{\sin\theta}(\hat{J}_y - \hat{L}_y)\sin\theta(\hat{J}_y - \hat{L}_y)\right]. \tag{17-40}$$

This Schrödinger equation does not separate into independent rotational (θ, ϕ), vibrational (R), and electronic $(x_3, y_3, z_3, \ldots, z_{n+2})$ parts because of (a) the occurrence of both R and the electronic coordinates in the potential function, (b) the occurrence of R in $\hat{T}_{\text{rot}}$, and (c) the occurrence of $\hat{L}_\alpha$ in $\hat{T}_{\text{rot}}$ (which gives rise to Coriolis coupling effects on the electrons). We can achieve a separation of rotation by neglecting the $\hat{L}_\alpha$ terms, and by setting $R = R_e$ (the equilibrium internuclear distance), in $\hat{T}_{\text{rot}}$. The approximate (rigid rotor) rotational kinetic energy operator obtained is

$$\hat{T}^0_{\text{rot}} = -\frac{1}{2\mu R_e{}^2}\left[\hat{J}_x{}^2 + \frac{1}{\sin\theta}\hat{J}_y\sin\theta\,\hat{J}_y\right]. \tag{17-41}$$

The separation of the vibrational and electronic coordinates is achieved by making the Born-Oppenheimer approximation discussed in Chapter 9.

17.3.2 The transformation properties of the rovibronic coordinates

The transformation properties of the rovibronic coordinates $(\theta, \phi, R, x_3, \ldots, z_{n+2})$ of a diatomic molecule can be determined from those of $(\xi_2, \ldots, \zeta_{n+2})$ by using Eqs. (17-12)–(17-17). We first consider the nuclear permutation (12), which is a symmetry operation only for homonuclear diatomic molecules, and then consider E^*, which is a symmetry operation for all diatomic molecules.

The effect of the nuclear permutation (12) on the nuclear coordinates in the (ξ, η, ζ) axis system can be written as

$$\begin{aligned}(12)(\xi_1, \eta_1, \zeta_1, \xi_2, \eta_2, \zeta_2) &= (\xi_1{}', \eta_1{}', \zeta_1{}', \xi_2{}', \eta_2{}', \zeta_2{}') &\quad (17\text{-}42)\\ &= (\xi_2, \eta_2, \zeta_2, \xi_1, \eta_1, \zeta_1) &\quad (17\text{-}43)\\ &= (-\xi_1, -\eta_1, -\zeta_1, -\xi_2, -\eta_2, -\zeta_2). &\quad (17\text{-}44)\end{aligned}$$

As a result of (12) the coordinates of the nuclei are interchanged see Eq. (17-43), and also since $\xi_1 = -\xi_2, \eta_1 = -\eta_2$, and $\zeta_1 = -\zeta_2$ for a homonuclear diatomic molecule the result in Eq. (17-44) follows. Using Eqs. (17-12) and (17-13) we have

$$(12)(\theta, \phi) = (\theta', \phi'), \qquad (17\text{-}45)$$

where

$$\theta' = \arccos[\zeta_2{}'(\xi_2{}'^2 + \eta_2{}'^2 + \zeta_2{}'^2)^{-1/2}], \qquad (17\text{-}46)$$

$$\phi' = \arccos[\xi_2{}'(\xi_2{}'^2 + \eta_2{}'^2)^{-1/2}], \qquad (17\text{-}47)$$

and

$$\phi' = \arcsin[\eta_2{}'(\xi_2{}'^2 + \eta_2{}'^2)^{-1/2}]. \qquad (17\text{-}48)$$

Substituting from Eqs. (17-42) and (17-44) we determine that

$$\cos\theta' = -\cos\theta, \qquad (17\text{-}49)$$

and

$$(\cos\phi', \sin\phi') = (-\cos\phi, -\sin\phi), \qquad (17\text{-}50)$$

so that

$$(\theta', \phi') = (\pi - \theta, \phi + \pi). \qquad (17\text{-}51)$$

Equation (17-51) follows from Eq. (17-49) since we must have $0 \leq \theta' \leq \pi$.

The result obtained here for the effect of (12) on θ and ϕ for a diatomic molecule can be appreciated by looking at Fig. 17-2. In Fig. 17-2a the molecule fixed axes are attached following the prescription given before Eq. (17-12). In Fig. 17-2b we have *first* permuted the nuclei according to (12) and *then* attached the molecule fixed axes according to the prescription given before Eq. (17-12). The z axis is reversed by (12) and the results in Eq. (17-51) immediately follow. Part of the prescription for attaching the (x, y, z) axes involves choosing $\chi = 0°$ and using this in Fig. 17-2b we find that the y axis is also reversed by (12). Equations (17-15) to (17-17) also lead to this result as we will see below when the transformation properties of the electronic coordinates are considered.

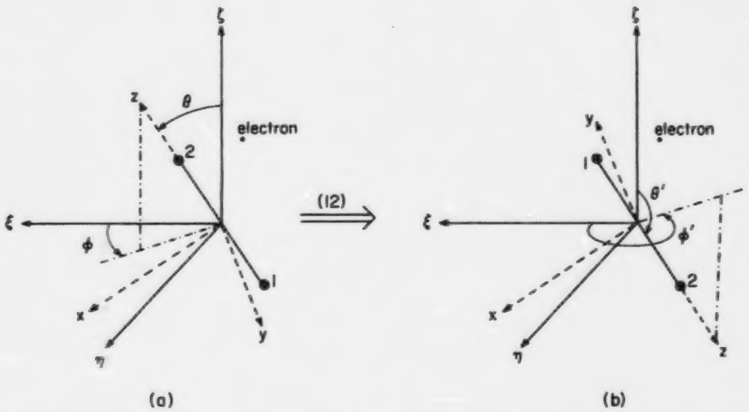

Fig. 17-2. The effect of the nuclear permutation (12) on the nuclei, an electron, and the molecule fixed (x, y, z) axes of a homonuclear diatomic molecule. The new values of the Euler angles (θ', ϕ') are related to the original values (θ, ϕ) by $\theta' = \pi - \theta$ and $\phi' = \phi + \pi$. $\chi = 0°$ in both figures by definition of the (x, y, z) axes.

Combining Eqs. (17-44) and (17-14) we see that the vibrational coordinate R is unaffected by (12) and we can write

$$(12)R = R' = R. \tag{17-52}$$

This can be seen by inspection of Fig. 17-2.

The electronic coordinates (ξ_i, η_i, ζ_i) are unaffected by the nuclear permutation (12), but the Euler angles are changed according to Eq. (17-51) so the (x_i, y_i, z_i) electronic coordinates are affected by (12). We can write

$$\begin{aligned}(12)x_i = x_i' &= \xi_i' \cos\theta' \cos\phi' + \eta_i' \cos\theta' \sin\phi' - \zeta_i' \sin\theta' \\ &= \xi_i \cos\theta \cos\phi + \eta_i \cos\theta \sin\phi - \zeta_i \sin\theta \\ &= x_i,\end{aligned} \tag{17-53}$$

where we have used Eq. (17-51). Similarly we obtain

$$(12)y_i = y_i' = -y_i \tag{17-54}$$

and

$$(12)z_i = z_i' = -z_i. \tag{17-55}$$

These results can be obtained from Fig. 17-2 since the y and z axes are reversed by (12) whereas the x axis is unaffected.

Summarizing the effect of (12) for a diatomic molecule we can write:

$$(12)(\theta, \phi, R, x_i, y_i, z_i) = (\pi - \theta, \phi + \pi, R, x_i, -y_i, -z_i). \tag{17-56}$$

The operation E^* is the inversion of the coordinates of all particles in the molecular center of mass and by definition we have

$$E^*(X_i, Y_i, Z_i) = (-X_i, -Y_i, -Z_i). \tag{17-57}$$

Using Eq. (9-40) we see that

$$E^*(\xi_i, \eta_i, \zeta_i) = (-\xi_i, -\eta_i, -\zeta_i) \tag{17-58}$$

for all particles in any molecule. Using this result together with Eqs. (17-12)–(17-17) we deduce that for a diatomic molecule

$$E^*(\theta, \phi, R, x_i, y_i, z_i) = (\pi - \theta, \phi + \pi, R, -x_i, y_i, z_i). \tag{17-59}$$

In Fig. 17-3 the effect of E^* for a diatomic molecule is drawn.

The operation $(12)^*$ is also a symmetry operation for homonuclear diatomic molecules, being the product of (12) and E^*. The effect of this operation on the rovibronic coordinates of a diatomic molecule is given by

$$(12)^*(\theta, \phi, R, x_i, y_i, z_i) = (\theta, \phi, R, -x_i, -y_i, -z_i). \tag{17-60}$$

This operation inverts the electronic coordinates through the origin of the molecule fixed axis system and does not alter the orientation of the molecule fixed axes in space. As discussed in general for centrosymmetric molecules in Chapter 4 [see Eq. (4-10)], the operation i from the molecular point group has the same effect as $(12)^*$ on the rovibronic coordinates of a homonuclear diatomic molecule.

Equations (17-56) and (17-60) apply to all homonuclear diatomic molecules, and Eq. (17-59) applies to all diatomic molecules. The effect of E^* on the rovibronic wavefunctions of a diatomic molecule leads to the ± label on the rovibronic levels, and (for a homonuclear diatomic molecule) the effect of (12) gives the a or s label. The effect of $(12)^*$ on the electronic wavefunctions gives the g or u label for the electronic states.

17.4 THE ISOMORPHIC HAMILTONIAN

As discussed in Section 17.1 above, in standard rotation-vibration theory we consider a linear molecule to have only two rotational degrees of freedom

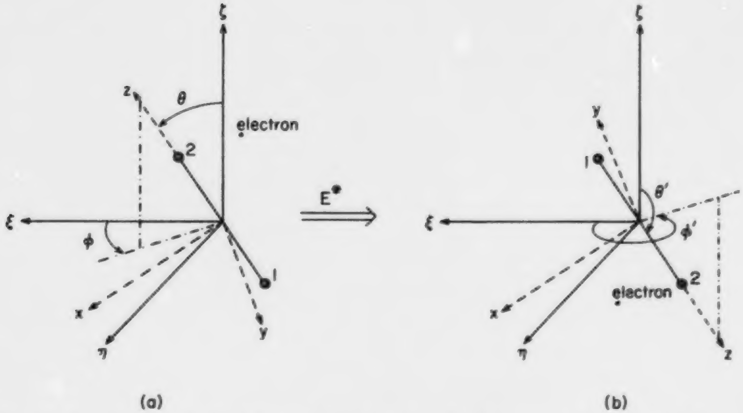

Fig. 17-3. The effect of E^* for a diatomic molecule. The new values of the Euler angles θ' and ϕ' are related to the original values by $\theta' = \pi - \theta$ and $\phi' = \phi + \pi$. Note the inversion of the electron coordinates in space at the origin of the (ξ, η, ζ) axis system.

corresponding to the two Euler angles θ and ϕ required to specify the direction of the molecular axis (the z axis) in space. Relative to the theory of nonlinear molecules outlined in Chapters 10 and 11, this lack of a third Euler angle causes some complications. We can use the Eckart conditions in Eqs. (17-1) and (17-2) to determine the Euler angles θ and ϕ. The Euler angle χ is usually chosen as a constant and in the derivation of the diatomic molecule Hamiltonian the choice $\chi = 0°$ was made. The most general choice would be to choose χ as a function of θ and ϕ. Because of this the direction cosine matrix elements [see Eq. (10-7)] will only depend on the two independent variables θ and ϕ. As a result of the absence of χ as a rotational variable the components of the angular momentum in the molecule fixed axis system for a linear molecule do not obey the commutation relations given in Eq. (10-92). Instead the commutation relations are more complicated [see, for example, Eqs. (17-31) and (17-32)], and the matrix elements involving these operators and the rotational eigenfunctions are not the same as for a nonlinear molecule (given in Table 11-1). The rotational kinetic energy operator for a linear molecule is also more complicated than that of a nonlinear molecule [see Eq. (10-150)] owing to the presence of extra angular factors [see Eq. (17-40) and note the presence of the $\sin\theta$ factors occurring in the second term].

A method has been devised for introducing the Euler angle χ as an independent variable for a linear molecule, and this is by the use of Hougen's isomorphic Hamiltonian [Hougen (1962a), Bunker and Papoušek (1969), Watson (1970), Howard and Moss (1971)]. The isomorphic Hamiltonian has one more degree of freedom than the true Hamiltonian and it has many eigenvalues that are not eigenvalues of the true Hamiltonian. However, it is easy to use a particular set of basis functions to diagonalize the isomorphic Hamiltonian so that these extra eigenvalues are not obtained. With the isomorphic Hamiltonian the components of the angular momentum along the molecule fixed axes have the commutation relations given in Eq. (10-92), and the rotational kinetic energy operator is simplified. Therefore, as a result of using the isomorphic Hamiltonian the linear molecule is treated in much the same way as the nonlinear molecule.

To obtain the isomorphic Hamiltonian for a linear molecule, χ is introduced as an independent variable, and the coordinates of the particles in the molecule are referred to an (x', y', z') axis system having Euler angles (θ, ϕ, χ) in the (ξ, η, ζ) axis system. As a result we introduce components of the rovibronic, electronic, and vibrational angular momentum, $\hat{\boldsymbol{J}}$, $\hat{\boldsymbol{L}}$, and $\hat{\boldsymbol{p}}$, respectively, along these axes (these components will be called $\hat{J}_x'$, $\hat{J}_y'$, etc.). If we initially choose $\chi = 0°$ in the true Hamiltonian (as for the diatomic molecule Hamiltonian discussed above) the (x', y', z') axes are rotated from the (x, y, z) axes about the $z(= z')$ axis through the angle χ (see Fig. 17-4). We have

$$(\hat{J}_x - \hat{p}_x - \hat{L}_x) = \cos\chi(\hat{J}_x' - \hat{p}_x' - \hat{L}_x') - \sin\chi(\hat{J}_y' - \hat{p}_y' - \hat{L}_y'), \qquad (17\text{-}61)$$

$$(\hat{J}_y - \hat{p}_y - \hat{L}_y) = \cos\chi(\hat{J}_y' - \hat{p}_y' - \hat{L}_y') + \sin\chi(\hat{J}_x' - \hat{p}_x' - \hat{L}_x'), \qquad (17\text{-}62)$$

and

$$(\hat{J}_z - \hat{p}_z - \hat{L}_z) = (\hat{J}_z' - \hat{p}_z' - \hat{L}_z') = 0. \qquad (17\text{-}63)$$

The $\hat{J}_x'$, $\hat{J}_y'$, and $\hat{J}_z'$ operators are the same as $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ given in Eqs. (10-84)–(10-86). The rotational kinetic energy operator (in cm^{-1}) of a linear molecule is transformed by this coordinate change to [see Eq. (83) of

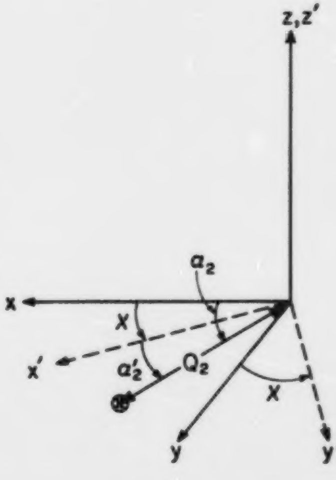

Fig. 17-4. Molecule fixed axes for a linear molecule. The (x, y, z) axes have Euler angles $(\theta, \phi, 0)$ in the (ξ, η, ζ) axis system, and the (x', y', z') axes used with the isomorphic Hamiltonian have Euler angles (θ, ϕ, χ) where χ is arbitrary. The bending vibration is described by an amplitude Q_2 and an angle $\alpha_2 = (\chi + \alpha_2')$ in the normal Hamiltonian, and by the coordinates Q_2 and α_2' in the isomorphic Hamiltonian.

Watson (1970)]

$$\hat{T}_{\text{rot}}^{\text{iso}} = B\hbar^{-2}[(\hat{J}_x{}' - \hat{p}_x{}' - \hat{L}_x{}')^2 + (\hat{J}_y{}' - \hat{p}_y{}' - \hat{L}_y{}')^2], \tag{17-64}$$

where the awkward angular factors have disappeared. The term U that is present for the nonlinear molecule [see Eq. (10-150)] is not present for the linear molecule. The coordinate change, from (x, y, z) to (x', y', z'), will not affect the form of the electronic kinetic energy operator $\hat{T}_e$, as we showed generally in the work leading to Eqs. (10-11) and (10-12), since the definition of χ is independent of the electronic coordinates. Also, since the vibrational coordinates are unaffected by the transformation, the vibrational kinetic energy operator $(\frac{1}{2}\sum_r \hat{P}_r{}^2)$ is also unchanged. The angular momenta $\hat{J}_x{}', \hat{J}_y{}'$, and $\hat{J}_z{}'$ in the isomorphic Hamiltonian satisfy the commutation relations given in Eq. (10-92) and, as for nonlinear molecules, they all commute with the components $\hat{p}_\alpha{}'$ and $\hat{L}_\alpha{}'$ of the vibrational and electronic angular momenta because they involve different sets of variables.

The isomorphic Hamiltonian $\hat{H}^{\text{iso}}$ commutes with $(\hat{J}_z{}' - \hat{p}_z{}' - \hat{L}_z{}')$ so that there exist simultaneous eigenfunctions of $\hat{H}^{\text{iso}}$ and $(\hat{J}_z{}' - \hat{p}_z{}' - \hat{L}_z{}')$. From Eq. (17-63) we see that the only eigenvalues of $\hat{H}^{\text{iso}}$ that are eigenvalues of the true Hamiltonian are those for which the corresponding eigenfunctions have eigenvalue zero for $(\hat{J}_z{}' - \hat{p}_z{}' - \hat{L}_z{}')$. Thus in setting up a zero order set of basis functions as products of rigid rotor (Φ_{rot}), harmonic oscillator (Φ_{vib}), and electron orbital (Φ_{elec}) functions we only use those basis functions for which $k = \Lambda + l$ where

$$\hat{J}_z{}'\Phi_{\text{rot}} = k\hbar\Phi_{\text{rot}}, \tag{17-65}$$

$$\hat{p}_z{}'\Phi_{\text{vib}} = l\hbar\Phi_{\text{vib}}, \tag{17-66}$$

and

$$\hat{L}_z{}'\Phi_{\text{elec}} = \Lambda\hbar\Phi_{\text{elec}}. \tag{17-67}$$

We now look at the form of these basis functions so that we can investigate their symmetry transformation properties.

17.4.1 The rovibronic wavefunctions

The (isomorphic) rigid rotor rotational Hamiltonian of a linear molecule is (in cm^{-1})

$$\hat{H}_{\text{rot}}^{\text{iso}} = B\hbar^{-2}(\hat{J}_x'^2 + \hat{J}_y'^2) = B\hbar^{-2}(\hat{\mathbf{J}}^2 - \hat{J}_z'^2), \tag{17-68}$$

so that the eigenvalues are

$$E_{\text{rot}}^{\text{iso}} = B[J(J+1) - k^2], \tag{17-69}$$

and the eigenfunctions are symmetric top functions [see Eq. (11-52)] which we write as

$$\Phi_{\mathrm{rot}}^{\mathrm{iso}} = [1/(2\pi)]^{1/2} S_{Jkm}(\theta,\phi)\exp(ik\chi). \tag{17-70}$$

The form of the function $S_{Jkm}(\theta,\phi)$ can be inferred from Eq. (11-15). This function involves a phase factor chosen such that the symmetric top function in Eq. (17-70) conforms to the phase choice of Eq. (11-52).

The vibrational Hamiltonian of a linear molecule involves $3N-5$ normal coordinates (there being three translational and two rotational degrees of freedom); there are $N-1$ nondegenerate normal coordinates and $N-2$ doubly degenerate bending normal coordinates as mentioned above. As a result the zero order harmonic oscillator wavefunctions are the products of $N-1$ one-dimensional and $N-2$ two-dimensional harmonic oscillator functions which we write as

$$\begin{aligned}\Phi_{\mathrm{vib}}^{\mathrm{iso}} &= \Phi_{v_1,\cdots,v_{2N-3}}(Q_1,\ldots,Q_{2N-3})\\ &\quad\times \exp(il_1\alpha_1{}')\exp(il_2\alpha_2{}')\cdots\exp(il_{N-2}\alpha'_{N-2})\end{aligned} \tag{17-71}$$

where Q_1 to Q_{N-2} are two-dimensional normal coordinates and Q_{N-1} to Q_{2N-3} are one-dimensional normal coordinates. The angles $\alpha_r{}'$ are as the α introduced in Eqs. (11-146)–(11-149) for a two-dimensional harmonic oscillator and here they are measured from the x' axis in the $x'y'$ plane (see Figs. 17-4 and 11-2). The total vibrational angular momentum about the linear axis (i.e., the eigenvalue of $\hat{p}_z{}'$) is given by

$$l\hbar = \sum_{r=1}^{N-2} l_r\hbar. \tag{17-72}$$

The electronic Hamiltonian of a linear molecule is solved in the same way as for a nonlinear molecule (see Chapter 9) and the zero order electronic wavefunction involves products of molecular orbitals (MO's), where each MO depends parametrically on the vibrational coordinates. When the nuclei are in the linear configuration the electronic Hamiltonian will commute with $\hat{L}_z{}'$, and Λ will be a good quantum number for the eigenstates. In this circumstance we can write

$$\Phi_{\mathrm{elec}}^{\mathrm{iso}} = \psi_{\mathrm{elec}}\exp(i\Lambda\chi_e') \tag{17-73}$$

where Ψ_{elec} is a function of interelectron distances, and $\chi_e{}'$ (a cylindrical angle about the z' axis) is the coordinate conjugate to $\hat{L}_z{}'$.

The rovibronic basis functions that we use to diagonalize $\hat{H}^{\mathrm{iso}}$ are the products of the functions in Eqs. (17-70), (17-71), and (17-73) with the restriction that

$$k = \Lambda + l. \tag{17-74}$$

This ensures that the eigenvalues of the isomorphic Hamiltonian obtained will only be those of the true Hamiltonian.

17.4.2 The symmetry classification of the basis set wavefunctions

In order to simplify the equations we will not look at the symmetry classification of the general basis set function just discussed but rather at the rotation–vibration wavefunction of HCN in its ground electronic state (this is a $\Lambda = 0$ state). This will enable us to see the relationship of the MS group to the molecular point group for a linear molecule fairly simply.

The rotation–vibration basis set functions for the isomorphic Hamiltonian of the HCN molecule in its ground electronic state are

$$\Phi_{\mathrm{rv}}^{\mathrm{iso}} = [1/(2\pi)]^{1/2} S_{Jkm}(\theta,\phi)\exp(ik\chi)\Phi_{v_1 v_2 v_3}(Q_1,Q_2,Q_3)\exp(il\alpha_2'), \quad (17\text{-}75)$$

where the two-dimensional bending vibration is numbered 2 in keeping with the established convention. We only use basis functions having $k = l$ [see Eq. (17-74)] which we can write as

$$\Phi_{\mathrm{rv}}^{\mathrm{iso}} = [1/(2\pi)]^{1/2} S_{JlM}(\theta,\phi)\exp(il\chi)\Phi_{v_1 v_2 v_3}(Q_1,Q_2,Q_3)\exp(il\alpha_2'), \quad (17\text{-}76)$$

and this is identical to

$$\Phi_{\mathrm{rv}}^{\mathrm{iso}} = [1/(2\pi)]^{1/2} S_{JlM}(\theta,\phi)\exp(il\alpha_2)\Phi_{v_1 v_2 v_3}(Q_1,Q_2,Q_3), \quad (17\text{-}77)$$

where we have introduced the angle α_2 given by

$$\alpha_2 = \alpha_2' + \chi \quad (17\text{-}78)$$

and α_2 is measured in the xy plane from the x axis [using the $\chi = 0°$ convention to define the (x, y, z) axis system] as shown in Fig. 17-4. We can also introduce the angle χ_e by writing

$$\chi_e = \chi_e' + \chi, \quad (17\text{-}79)$$

and the rovibronic wavefunction of a $\Lambda \neq 0$ state would involve the product $\exp(il\alpha_2)\exp(i\Lambda\chi_e)$.

As an aside, we note here that the rotation-vibration wavefunction of HCN given in Eq. (17-77) depends on the coordinates $(\theta,\phi,Q_1,Q_2,Q_3,\alpha_2)$. We have introduced α_2 as a vibrational coordinate, associated with the bending vibration ν_2, but it is clear that for constant values of (Q_1,Q_2,Q_3) [where $Q_2 \neq 0$], variation of α_2 describes a rotation of a rigid HCN molecule around the z axis [see Fig. 17-4]. That is, α describes the motion which is described by the angle χ in the HBJ approach.

Before discussing the symmetry classification of this rotation-vibration function we must introduce the symmetry groups of linear molecules. The point group of a linear molecule is $\boldsymbol{D}_{\infty h}$ if it is centrosymmetric, otherwise it is $\boldsymbol{C}_{\infty v}$.

Both of these groups have an infinite number of elements. The MS group of a molecule such as HCN that has $\boldsymbol{C}_{\infty\mathrm{v}}$ point group symmetry is called $\boldsymbol{C}_{\infty\mathrm{v}}(\mathrm{M})$ and it consists of the two elements E and E^*. The MS group of a molecule such as CO_2 that has $\boldsymbol{D}_{\infty\mathrm{h}}$ point group symmetry is called $\boldsymbol{D}_{\infty\mathrm{h}}(\mathrm{M})$ and it consists of the four elements $E, (p), E^*$ and $(p)^*$, where (p) is the permutation of all pairs of identical nuclei that, in the equilibrium configuration, are located symmetrically about the nuclear center of mass. The operation $(p)^*$ is therefore identical to the operation $\hat{O}_i$ introduced in Eq. (4-7). The character table of the group $\boldsymbol{C}_{\infty\mathrm{v}}(\mathrm{M})$ is given in Table A-17 and its two irreducible representations are labeled + (or Σ^+) and − (or Σ^-) as the character under E^* (i.e., the parity) is +1 or −1. The character table of the group $\boldsymbol{D}_{\infty\mathrm{h}}(\mathrm{M})$ is given in Table A-18. The irreducible representations are labeled +s (or $\Sigma_g{}^+$), +a (or $\Sigma_u{}^+$), −s (or Σ_u^-) and −a (or Σ_g^-), where the + or − depends on the character under E^*, the s or a on the character under (p), and the g or u on the character under $(p)^*$. We see that for a linear rigid molecule the MS group and the molecular point group are not isomorphic, unlike the situation for a nonlinear rigid molecule. We will now discuss the use of the MS group and molecular point group for classifying the rotation–vibration wavefunction of HCN given in Eq. (17-77).

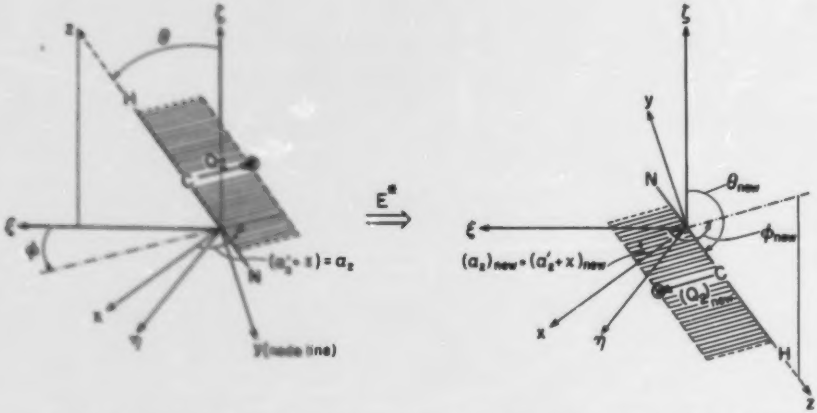

Fig. 17-5. The effect of E^* on the coordinates θ, ϕ, Q_2, and α_2 for the HCN molecule. The directions of the x and y axes in space are reversed by E^*.

The rotation-vibration wavefunction of HCN given in Eq. (17-77) can be classified in the MS group $\boldsymbol{C}_{\infty\mathrm{v}}(\mathrm{M})$. We can do this because the coordinates occurring in the wavefunction, $\theta, \phi, \alpha_2, Q_1, Q_2$, and Q_3, all have well-defined transformation properties under the elements of the group $\boldsymbol{C}_{\infty\mathrm{v}}(\mathrm{M})$. The transformation properties of the coordinates under the effect of E^* are [see Fig. 17-5 and Eq. (17-59)]

$$E^*(\theta, \phi) = (\theta_{\mathrm{new}}, \phi_{\mathrm{new}}) = (\pi - \theta, \phi + \pi), \tag{17-80}$$

$$E^*\alpha_2 = (\alpha_2)_{\mathrm{new}} = \pi - \alpha_2, \tag{17-81}$$

and

$$E^*(Q_1, Q_2, Q_3) = (Q_1, Q_2, Q_3). \tag{17-82}$$

The z axis, the y axis, and the direction of the bending displacement in space (but not the x axis from which α_2 is measured) are all reversed by E^*. The coordinates Q_1 and Q_3 transform like $(\Delta z_H - \Delta z_C)$ and $(\Delta z_C - \Delta z_N)$, and are unaffected by E^*; Q_2 is the amplitude of the degenerate vibration and is unaffected by a symmetry operation. For a $\boldsymbol{D}_{\infty h}$ linear molecule such as CO_2 it can be shown that [see Eqs. (17-56) and (17-60)]

$$(p)(\theta, \phi, \alpha_2) = (\pi - \theta, \phi + \pi, -\alpha_2) \tag{17-83}$$

and

$$(p)^*(\theta, \phi, \alpha_2) = (\theta, \phi, \alpha_2 + \pi). \tag{17-84}$$

From Eqs. (17-80)–(17-82) we deduce that the effect of E^* on the rotation–vibration wavefunction of HCN is

$$E^*\Phi_{rv}^{iso} = [1/(2\pi)]^{1/2} S_{Jlm}(\pi - \theta, \phi + \pi) \exp[il(\pi - \alpha_2)] \Phi_{v_1 v_2 v_3}(Q_1, Q_2, Q_3). \tag{17-85}$$

Table 12-1 shows that the equivalent rotation $R_{\pi/2}^{\pi}$ changes the "usual" Euler angles (θ, ϕ, χ) for a nonlinear molecule in exactly the same way as E^* changes (θ, ϕ, α_2) [Eqs. (17-80) and (17-81)]. The factor $[1/(2\pi)]^{1/2} S_{JlM}(\theta, \phi) \exp(il\alpha_2)$ on the right hand side of Eq. (17-77) is a symmetric top function $|J, l, m\rangle$ depending on (θ, ϕ, α_2) [see Eq. (17-70)], and we can use Eq. (12-47) to deduce that

$$E^*\Phi_{rv}^{iso} = (-1)^{J+l} [1/(2\pi)]^{1/2} S_{J-lm}(\theta, \phi) \exp(-il\alpha_2) \Phi_{v_1 v_2 v_3}(Q_1, Q_2, Q_3). \tag{17-86}$$

Thus for $l = 0$ states the rovibronic states with J even are + and those with J odd are −. For $l \neq 0$ states we must form sum and difference functions in order that the functions transform irreducibly, i.e., we form (using an obvious notation)

$$\Phi_{rv}^{\pm} = (|J, |l|, m, v_1, v_2, v_3\rangle \pm |J, -|l|, m, v_1, v_2, v_3\rangle)/\sqrt{2}. \tag{17-87}$$

The Φ_{rv}^{+} (or Φ_{rv}^{-}) function is + (or −) for $J + l$ even and − (or +) for $J + l$ odd. In general the rovibronic states of a $\boldsymbol{C}_{\infty v}$ molecule can be classified as being + or − in its MS group, and for a $\boldsymbol{D}_{\infty h}$ molecule as +s, −s, +a, or −a in its MS group.

As well as classifying the rotation–vibration wavefunctions we wish to classify the rotation and vibration wavefunctions separately. The rotation and vibration wavefunctions of HCN in the ground electronic state are [from Eqs. (17-70), (17-71), and (17-76)]

$$\Phi_{rot}^{iso} = [1/(2\pi)]^{1/2} S_{Jlm}(\theta, \phi) \exp(il\chi) \tag{17-88}$$

and

$$\Phi_{\mathrm{vib}}^{\mathrm{iso}} = \Phi_{v_1 v_2 v_3}(Q_1, Q_2, Q_3)\exp(il\alpha_2'). \tag{17-89}$$

To determine the transformation properties of these functions in the MS group we must determine the transformation properties of the rotational and vibrational coordinates $\theta, \phi, \chi, Q_1, Q_2, Q_3$, and α_2' under the effect of the elements E and E^* of the MS group. The transformation properties of θ, ϕ, Q_1, Q_2, and Q_3 present no problem but χ and α_2' do present a problem. This is because there is no Eckart condition that defines χ. Hence, after performing E or E^* we do not know where to locate the $x'y'$ axes and we do not know the values of χ and α_2'. The transformation properties of the angle $\alpha_2 = \chi + \alpha_2'$ are well defined, see Eq. (17-81), since this does not depend on the orientation of the $x'y'$ axes. The rotation and vibration functions of HCN do not, therefore, have separately determinable parities. This problem occurs for all linear molecules since the rotational angle χ and the vibronic variables α_r' and χ_e' do not have determinable transformation properties under the effect of a nuclear permutation or permutation–inversion. On the other hand the Euler angle χ has well-defined transformation properties under the elements of the molecular point group. This is because the elements of the molecular point group are defined as doing nothing at all to the Euler angles.[2] Since χ is unchanged after a point group operation the location of the $x'y'$ axes after a point group operation is defined and the transformation properties of the vibronic variables α_2' and χ_e' are defined. Thus the vibronic wavefunctions of a linear molecule can be classified in the appropriate molecular point group. For a $\boldsymbol{C}_{\infty\mathrm{v}}$ molecule the vibronic states can be of species $\Sigma^+, \Sigma^-, \Pi, \Delta$, etc., and for a $\boldsymbol{D}_{\infty\mathrm{h}}$ molecule there is an additional g or u label. Just as for nonlinear molecules the molecular point group is not a symmetry group of the rovibronic Hamiltonian (since the components $\hat{J}_\alpha'$ are not transformed by its elements, whereas $\hat{p}_\alpha'$ and $\hat{L}_\alpha'$ are transformed), and it is not the correct group to use for classifying rovibronic states.

The vibrational and electronic wavefunctions can be classified in the molecular point group for a linear molecule. The elements of the $\boldsymbol{D}_{\infty\mathrm{h}}$ point group are

$$E(= C_\infty{}^0), C_\infty{}^\varepsilon, C_2^{(\varepsilon/2)}, \sigma_{\mathrm{v}}^{(\varepsilon/2)}, \text{ and } S_\infty{}^\varepsilon, \tag{17-90}$$

where

$C_\infty{}^\varepsilon$ is a rotation (in a right handed sense) of the vibronic variables about the z' axis through the angle ε,

$C_2^{(\varepsilon/2)}$ is a twofold rotation of the vibronic variables about an axis that makes an angle $(\varepsilon/2)$ (measured in a right handed sense about the z' axis) with the x' axis,

$\sigma_{\mathrm{v}}^{(\varepsilon/2)}$ is a reflection of the vibronic variables in a plane containing the z' axis and the axis just described that makes an angle of $(\varepsilon/2)$ with the x' axis, and

---

[2] It is more correct to say that the Euler angles are not transformed by the elements of the molecular point group.

S_∞^ε is the product of C_∞^ε and the reflection (σ_h) of the vibronic variables in the $x'y'$ plane, i.e.,

$$S_\infty^\varepsilon = C_\infty^\varepsilon \sigma_h. \tag{17-91}$$

Note that in the $\boldsymbol{D}_{\infty h}$ point group

$$S_\infty^0 = \sigma_h \tag{17-92}$$

and

$$S_\infty^\pi = i. \tag{17-93}$$

In the preceding definitions the angles ε can assume any value (mod 2π) in the range $0 \le \varepsilon \le 2\pi$ independently of each other; for the $\boldsymbol{C}_{\infty v}$ point group the elements $C_2^{(\varepsilon/2)}$ and S_∞^ε do not occur.

The classification of the vibrational wavefunctions of a linear molecule in the appropriate point group is straightforward. The effects of the operations of Eq. (17-90) on the vibrational angles α_r' for the degenerate vibrations are

$$C_\infty^\varepsilon \alpha_r' = S_\infty^\varepsilon \alpha_r' = \alpha_r' + \varepsilon \tag{17-94}$$

and

$$C_2^{(\varepsilon/2)} \alpha_r' = \sigma_v^{(\varepsilon/2)} \alpha_r' = -\alpha_r' + \varepsilon. \tag{17-95}$$

Electronic cylindrical angles (measured from the x' axis) will transform in the same way. Using the point group we can classify the vibrational and electronic wavefunctions of a linear molecule. The two-dimensional vibrational wavefunctions of the HCN molecule [see Eq. (17-89)] are transformed as

$$C_\infty^\varepsilon \Phi_{v_2}(Q_2)\exp(il\alpha_2') = \exp(il\varepsilon)\Phi_{v_2}(Q_2)\exp(il\alpha_2') \tag{17-96}$$

and

$$\sigma_v^{(\varepsilon/2)} \Phi_{v_2}(Q_2)\exp(il\alpha_2') = \exp(il\varepsilon)\Phi_{v_2}(Q_2)\exp(-il\alpha_2'). \tag{17-97}$$

Thus the pair of functions $(|v_2, l\rangle, |v_2, -l\rangle)$ have character $2\cos l\varepsilon$ (i.e., $e^{il\varepsilon} + e^{-il\varepsilon}$) under C_∞^ε, and they have a character of 0 if $l \neq 0$ under $\sigma_v^{(\varepsilon/2)}$. For a $\boldsymbol{D}_{\infty h}$ molecule such as CO_2 we have

$$S_\infty^\pi |v_2, l\rangle = (-1)^l |v_2, l\rangle, \tag{17-98}$$

so that functions with l even are g and those with l odd are u, and the species of the functions depends on l as given in Table 17-1 (see Table A-20 for the $\boldsymbol{D}_{\infty h}$ character table). The symmetry classification of the vibrational states associated with the nondegenerate vibrations presents no special problems.

Table 17-1

The species of the bending wavefunctions of CO_2 in the $\boldsymbol{D}_{\infty h}$ point group[a]

l	$\Gamma(\lvert v_2, l\rangle)$
0	$\Sigma_g{}^+$
± 1	Π_u
± 2	Δ_g
± 3	Φ_u
$\vdots$	$\vdots$

[a] For a $\boldsymbol{C}_{\infty v}$ molecule such as HCN the g and u subscripts should be omitted.

For a molecule of $\boldsymbol{D}_{\infty h}$ point group symmetry, we define the extended molecular symmetry group (EMS group) $\boldsymbol{D}_{\infty h}(\mathrm{EM})$ to have the following elements

$$E(=E_0), E_\varepsilon, (p)_\varepsilon, E_\varepsilon{}^*, \text{ and } (p)_\varepsilon{}^*. \tag{17-99}$$

Analogously, the elements of $\boldsymbol{C}_{\infty v}(\mathrm{EM})$ are

$$E(=E_0), E_\varepsilon, \text{ and } E_\varepsilon{}^*. \tag{17-100}$$

In Eq. (17-99) and (17-100), the subscripts ε can assume any value (mod 2π) in the range $0 \le \varepsilon \le 2\pi$ independently of each other. A general element O_ε of the EMS group is defined as follows: (i) The effect of O_ε on the spatial coordinates of the nuclei and electrons in the molecule [i.e., on the (ξ_i, η_i, ζ_i) coordinates] is the same as that of the element O of the MS group. (ii) The effect of O_ε on the Euler angles θ and ϕ is the same as the effect of O of the MS group. (iii) The effect of O_ε on the Euler angle χ is defined by the value of ε according to the following rules:

$$E_\varepsilon \chi = \chi - \varepsilon, \tag{17-101}$$

$$(p)_\varepsilon \chi = 2\pi - \chi - \varepsilon, \tag{17-102}$$

$$E_\varepsilon{}^* \chi = \pi - \chi - \varepsilon, \tag{17-103}$$

$$(p)_\varepsilon{}^* \chi = \pi + \chi - \varepsilon. \tag{17-104}$$

This completely defines the elements of the EMS group.

The transformation properties of χ have been defined in such a manner that each element of the EMS group has the same effect on the vibronic variables $\alpha_r{}'$ and $\chi_e{}'$ as an element in the molecular point group. From parts (i) and (ii) of the definition of O_ε we see that the effect of O_ε on the rovibronic angles α_r

and χ_e must be the same as the effect[3] of O. The effect of O on χ is defined by part (iii) of the definition of O_ε, and thus we can determine the transformation properties of the vibronic coordinates $\alpha_r{}'(= \alpha_r - \chi)$ and $\chi_e{}'(= \chi_e - \chi)$. The results for $\alpha_r{}'$ and $\chi_e{}'$ are the same, and for $\alpha_r{}'$ we have

$$E_\varepsilon \alpha_r{}' = \alpha_r{}' + \varepsilon, \tag{17-105}$$

$$(p)_\varepsilon \alpha_r{}' = -\alpha_r{}' + \varepsilon, \tag{17-106}$$

$$E_\varepsilon{}^* \alpha_r{}' = -\alpha_r{}' + \varepsilon, \tag{17-107}$$

$$(p)_\varepsilon{}^* \alpha_r{}' = \alpha_r{}' + \varepsilon. \tag{17-108}$$

As can be seen from the definition of the effect of O_ε, together with the results of Eqs. (17-105)–(17-108), each element of the EMS group can be written as the product of a molecular point group operation that affects only the vibronic variables ($Q_r, \alpha_r{}'$, and $\chi_e{}'$), a rotation operation that affects only the Euler angles (see Table 12-1), and a nuclear spin permutation. We can, therefore, write each element of the EMS group as follows:

$$E_\varepsilon = C_\infty{}^\varepsilon R_z^{-\varepsilon} p_0, \tag{17-109}$$

$$(p)_\varepsilon = C_2^{(\varepsilon/2)} R^\pi_{\varepsilon/2} p_{\mathrm{ns}}, \tag{17-110}$$

$$E_\varepsilon{}^* = \sigma_v^{(\varepsilon/2)} R^\pi_{(\pi+\varepsilon)/2} p_0, \tag{17-111}$$

$$(p)_\varepsilon{}^* = S_\infty{}^\varepsilon R_z^{\pi-\varepsilon} p_{\mathrm{ns}} \quad [(p)_\pi{}^* = S_\infty{}^\pi R_z{}^0 p_{\mathrm{ns}} = i p_{\mathrm{ns}}], \tag{17-112}$$

where p_{ns} is the permutation of the nuclear spin coordinates of the nuclei that are permuted by (p). Each of these equations is of the form of Eq. (4-5) which was developed for nonlinear molecules. Since the EMS group and the point group of a linear molecule are isomorphic [the 1:1 relation between the elements follows from Eqs. (17-109)–(17-112)] we use the same character table and irreducible representation labels for each (see Tables A-19 and A-20). Since each element of the EMS group transforms the vibronic variables in the same way as its partner in the molecular point group the vibronic wavefunctions can equally well be classified in the EMS group as in the molecular point group and the same results (such as in Table 17-1) will be obtained. The rotational wavefunctions of a linear molecule can also be classified in the EMS group and the results for a $\boldsymbol{D}_{\infty\mathrm{h}}$ molecule are given in Table 17-2. For a $\boldsymbol{C}_{\infty\mathrm{v}}$ molecule the g subscripts should be omitted. The species of the rovibronic functions are obtained by multiplying the rotational and vibronic species together bearing in mind the restriction imposed by Eq. (17-74).

The effect of a general element O_ε of the EMS group of a linear molecule on a rovibronic wavefunction will be exactly the same as the effect of the element O of the MS group. This follows from part (i) of the definition of O_ε. This means that the elements of the EMS group leave the rovibronic Hamiltonian invariant and that we can classify the rovibronic states in the EMS group. We deduce

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[3] Given in Eqs. (17-81), (17-83), and (17-84).

Table 17-2

The Species of the rotational wavefunctions of a $\boldsymbol{D}_{\infty h}$ molecule in the EMS group $\boldsymbol{D}_{\infty h}$(EM)[a]

k		$\Gamma(\lvert Jkm\rangle)$
0	(J even)	Σ_g^+
	(J odd)	Σ_g^-
±1		Π_g
±2		Δ_g
±3		Φ_g
⋮		⋮

[a] For a molecule of $C_{\infty v}$ symmetry the classification in $C_{\infty v}$(EM) gives the same results with the g subscripts omitted.

that the rovibronic wavefunctions of a $\boldsymbol{D}_{\infty h}$ molecule can only transform as one of the four one-dimensional irreducible representations $\Sigma_g{}^+$, $\Sigma_u{}^+$, $\Sigma_g{}^-$, and $\Sigma_u{}^-$ of the EMS group $\boldsymbol{D}_{\infty h}$(EM). Similarly for a $C_{\infty v}$ molecule the rovibronic wavefunctions can only transform as Σ^+ or Σ^- of $C_{\infty v}$(EM). The classification of a rovibronic wavefunction of a $\boldsymbol{D}_{\infty h}$ molecule as $\Sigma_g{}^+, \Sigma_u{}^+, \Sigma_g{}^-$, and $\Sigma_u{}^-$ is equivalent to the standard (MS group) notation of +s, +a, −a, and −s, respectively; for a $C_{\infty v}$ molecule Σ^+ and Σ^- are equivalent to the standard notations + and −. In Fig. 17-6 examples of the application of this classification scheme to rovibronic states are given.

17.5 ENERGY LEVEL LABELS

17.5.1 Parity and the *e*/*f* label

For singlet electronic states of linear molecules the nondegenerate vibronic states (such as the $\Sigma_g{}^+$ and $\Sigma_g{}^-$ vibronic states in Figure 17-6) have rotational levels that are uniquely identified by giving their $J = N$ value, but for the degenerate vibronic states (such as the Π_g and Δ_g vibronic states in Figure 17-6) there is a pair of levels for each $J = N$ value. These energy level pairs are split apart by Coriolis coupling, and this is called Λ-type doubling, *l*-type doubling, or *k*-type doubling depending on the circumstances [see, for example, Johns (1965)]. The pairs of split levels have opposite parity which alternates as J increases. In Figure 17-6 we have chosen to represent the effect of the Coriolis coupling as causing the lower levels for J even (odd) to have parity +(−), but

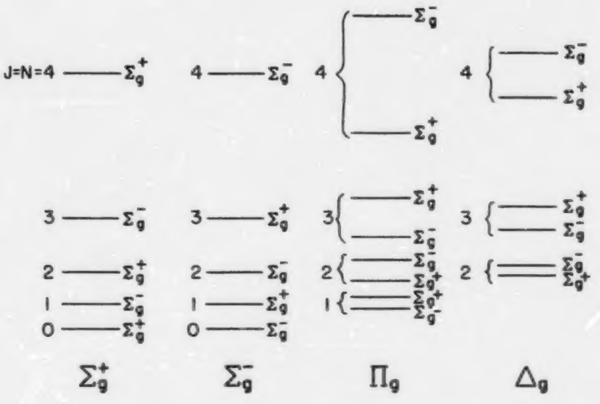

Fig. 17-6. The symmetries of the rovibronic states (rotational levels) of Σ_g^+, Σ_g^-, Π_g, and Δ_g vibronic states of a $\boldsymbol{D}_{\infty h}$ molecule in a singlet electronic state. The rovibronic symmetry labels Σ_g^+, Σ_u^+, Σ_g^-, and Σ_u^- are equivalent to the standard (MS group) labels +s, +a, −a, and −s, respectively. For u vibronic states the g subscripts should be replaced by u subscripts, and for a $\boldsymbol{C}_{\infty v}$ molecule the subscripts should be omitted. In this figure we have chosen to represent the effect of the *l*-type (or Λ-type) doubling in the degenerate vibronic states as causing the lower levels for *J* even (odd) to have parity +(−), but this splitting could be inverted. [See Herzberg (1991b), p. 572.]

this splitting could be inverted. For a state having $S \neq 0$ each of these levels is further split into a multiplet having the same N value and parity but different J value. The quantum number J gives the sum of the rovibronic and electron spin angular momenta [see Eq. (10-97)]. It is useful to have a unique way of labeling the levels that are split apart, and for the interpretation of experimental spectra it is helpful to introduce a notation that allows us to label, as a set, all the lower-energy levels in the pairs, and, separately, all the higher-energy levels. The sets are labeled *c* and *d* in some circumstances and *e* and *f* in others. There has been confusion in the past caused by the awkward definitions used for the labels, but this has now been rectified.

The recommended *e*/*f* labeling scheme is that introduced by Brown, Hougen, Huber, Johns, Kopp, Lefebvre-Brion, Merer, Ramsay, Rostas, and Zare (1975), and it is defined for vibronic states of any multiplicity (even or odd) so that it can be used whether J is integral or half-integral. For molecules that have an even number of electrons so that S and J are integral, the *e* levels are those that have parity $+(-1)^J$ and the *f* levels those that have parity $-(-1)^J$. For half-integral J values [i.e., for molecules with an odd number of electrons], *e* levels have parity $+(-1)^{J-1/2}$ and *f* levels have parity $-(-1)^{J-1/2}$. For the Π_g and Δ_g vibronic states in Fig. 17-6 the lower J components are *e* levels and the upper components are *f* levels; the splitting could be inverted with the *f* level below the *e* level for each J.

The recommended c/d labeling scheme is that proposed by Watson (1991), and it is useful whenever the integral quantum number N is well defined. In this definition the c levels have parity $+(-1)^N$ and d levels have parity $-(-1)^N$. This is the definition adopted by Herzberg (1989) for singlet states of diatomic molecules and it is the notation customarily used by rotation-vibration spectroscopists for linear molecules. In an electronic state with $S > 0$, the fine structure energies with different J values that originate from the spin-splitting of a rovibronic energy level with a given N value and parity will all have the same c/d label but not the same e/f label. In a singlet electronic state we have $N = J$, and the correlation between e/f and c/d is simply $e \equiv c$ and $f \equiv d$, so for the Π_g and Δ_g vibronic states in Fig. 17-6, the lower J components are c levels and the upper components are d levels.

Table 17-3

Generating operations for the point groups of linear molecules

	R_+	R'_+	R_-
$\boldsymbol{C}_{\infty\mathrm{v}}$	$C_\infty{}^\varepsilon$		$\sigma_{\mathrm{v}}^{(0/2)}$
$\boldsymbol{D}_{\infty\mathrm{h}}$	$C_\infty{}^\varepsilon$	i	$C_2^{(0/2)}$

The group operations are described by means of a right-handed axis system $x'y'z'$. The point group operations are defined in connection with Eq. (17-90).

The rotation-vibration energy levels of a linear molecule in an isolated totally symmetric singlet (${}^1\Sigma^+$ or ${}^1\Sigma_g^+$) electronic ground state are often the subject of experimental study; such electronic states have $\Lambda = 0$. The rest of this section is concerned with such an electronic state for which the rotation-vibration energies are obtained by diagonalizing the matrix representation of the Watsonian of the isomorphic Hamiltonian [see, for example, Papoušek and Aliev (1982)] in a basis of functions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}$ [see Eq. (12-73)]. They can be symmetry classified in the MS (or EMS) group in the manner described for symmetric top molecules by Eqs. (12-74)-(12-82) together with Tables 12-13 and 12-14 [Hougen (1962c); Hegelund, Rasmussen, and Brodersen (1973)]. In order to carry out the symmetry classification, we must first choose generating operations for the point groups $\boldsymbol{C}_{\infty\mathrm{v}}$ and $\boldsymbol{D}_{\infty\mathrm{h}}$. A common choice of these operations is given in Table 17-3, where we have used the notation for $\boldsymbol{C}_{\infty\mathrm{v}}$ and $\boldsymbol{D}_{\infty\mathrm{h}}$ operations introduced in Eq. (17-90). In the rest of this section N is called J again since we only deal with singlet states.

Table 17-4

Transformation properties of the linear molecule basis functions

$\boldsymbol{C}_{\infty\mathrm{v}}$	g_{rv}	$= 0$
	ρ	$= J + \sum_t l_t + 2t$
$\boldsymbol{D}_{\infty\mathrm{h}}$	g_{rv}	$= 0$
	η	$= \sum v_{\mathrm{u}} + 2t$
	ρ	$= J + \sum v_{\Sigma_{\mathrm{u}}^{+}} + 2t$

The sum $\sum_t l_t$ runs over all degenerate normal modes of the molecule in question. The summations $\sum v_{\mathrm{u}}$ and $\sum v_{\Sigma_{\mathrm{u}}^{+}}$ represent sums over the v quantum numbers belonging to nondegenerate normal modes with u-type symmetry or symmetry Σ_{u}^{+}, respectively. The quantity t is an integer determined independently for the quantum numbers η and ρ, so that $\eta = 0$ or 1 and $\rho = 0$ or 1.

The basis functions $\Phi_{\mathrm{rv}}^{(V,L,J,k,m)}$ will transform under the EMS group partners of the generating operations R_{+}, R'_{+}, and R_{-} in Table 17-3 as given by Eqs. (12-74)-(12-76), and the quantities g_{rv}, η, and ρ defined by Table 17-4. It follows from Eq. (17-74) [in which we set $\Lambda = 0$ in the present case] that we have $g_{\mathrm{rv}} = 0$, and thus the rotation-vibration basis functions for a linear molecules are always Type II functions [see Eqs. (12-78)-(12-82)] given by

$$\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)} = \frac{1}{\sqrt{2}}\left[\Phi_{\mathrm{rv}}^{(V,L,J,k,m)} + (-1)^{\rho+\tau}\,\Phi_{\mathrm{rv}}^{(V,-L,J,-k,m)}\right], \qquad (17\text{-}113)$$

where $\tau = 0$ or 1, if at least one $l_t \neq 0$, and

$$\Phi_{\mathrm{rv}}^{(V,0,J,0,m,\tau)} = \Phi_{\mathrm{rv}}^{(V,0,J,0,m)} \qquad (17\text{-}114)$$

where, by definition, $\tau = \rho$, if all $l_t = 0$. The transformation properties of the linear molecule basis functions under the EMS group partners of the generating operations for $\boldsymbol{C}_{\infty\mathrm{v}}$ and $\boldsymbol{D}_{\infty\mathrm{h}}$ are given by Eqs. (12-79)-(12-81).

For $\boldsymbol{C}_{\infty\mathrm{v}}$ molecules, it follows from Eq. (17-111) that the EMS group partner of the generating operation $R_{-} = \sigma_{\mathrm{v}}^{(0/2)}$ is E_0^{*}, which has the same effect on the rovibronic wavefunctions as the MS group operation E^{*}. Thus Eq. (12-81) can be reinterpreted as

$$E^{*}\,\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)} = (-1)^{\tau}\,\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}. \qquad (17\text{-}115)$$

The parity of the function $\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}$ is $(-1)^{\tau}$. Basis functions with $\tau = 0$ have '+' symmetry in the MS group $\boldsymbol{C}_{\infty\mathrm{v}}(\mathrm{M})$, and basis functions with $\tau = 1$

have '−' symmetry [see Table A-17], so that levels with $J+\tau$ even are c or e levels, and levels with $J+\tau$ odd are d or f levels.

For $\boldsymbol{D}_{\infty\mathrm{h}}$ molecules, we have from Eq. (17-112) that $R'_{+}=i$ has the EMS group partner $(p)^*_\pi$, and from Eq. (17-110) that $R_{-}=C_2^{(0/2)}$ has the EMS group partner $(p)_0$. The two EMS group operations have the same effect on the rovibronic wavefunction as $(p)^*$ and (p), respectively. From Eqs. (12-80) and (12-81) we obtain

$$(p)^*\,\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}=(-1)^{\eta}\,\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)} \tag{17-116}$$

and

$$(p)\,\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}=(-1)^{\tau}\,\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}, \tag{17-117}$$

so that

$$E^*\,\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}=(-1)^{\eta+\tau}\,\Phi_{\mathrm{rv}}^{(V,L,J,k,m,\tau)}. \tag{17-118}$$

Consequently, the four irreducible representations +s, −a, −s, and +a in the MS group $\boldsymbol{D}_{\infty\mathrm{h}}(\mathrm{M})$ [see Table A-18] correspond to $(\eta,\tau)=(0,0)$, $(0,1)$, $(1,0)$, and $(1,1)$, respectively; levels with $J+\eta+\tau$ even are c or e levels, and levels with $J+\eta+\tau$ odd are d or f levels.

17.5.2 The correlation between the energy level labels of linear and bent triatomic molecules

For a linear triatomic molecule the levels are labeled $(J,N,e/f,v_1,v_2^{\mathrm{linear}},l,v_3)$, whereas for a bent molecule the levels are labeled $(J,N,K_a,K_c,v_1,v_2^{\mathrm{bent}},v_3)$, where $K_a+K_c=N$ or $N+1$. For a quasilinear molecule it is a matter of taste which set of labels is used. The four quantum numbers (J,N,v_1,v_3) are defined in the same way for linear and bent molecules, but the labels v_2^{bent}, v_2^{linear}, $K_a=|k_a|$ and l require special discussion.

From Section 17.2 we see that

$$l=k_a, \tag{17-119}$$

and these quantum numbers both give the value of the projection (in units of $\hbar$) of the rovibronic angular momentum on the a axis of the molecule (the a axis being the axis of smallest moment of inertia which coincides with the molecular axis when the molecule is linear).

The correlation between the principal bending quantum numbers v_2^{bent} and v_2^{linear} is where the problem lies since they are not the same. For a bent molecule, the lowest bending energy (or energy doublet if $K_a>0$) with a given K_a value is labeled $v_2^{\mathrm{bent}}=0$, the next one (in order of increasing energy) is labeled $v_2^{\mathrm{bent}}=1$, the next one $v_2^{\mathrm{bent}}=2$, and so on. For a linear molecule, the energies in this stack have $|l|=K_a$ [Eq. (17-119)]. The lowest energy (or energy doublet for $|l|>0$) has $v_2^{\mathrm{linear}}=|l|$, the next one has $v_2^{\mathrm{linear}}=|l|+2$, the next one has $v_2^{\rm linear} = |l|+4$ and so on [see Section 11.3.2]. Comparison of the two labeling schemes gives

$$v_2^{\rm linear} = 2v_2^{\rm bent} + K_a \tag{17-120}$$

or, conversely,

$$v_2^{\rm bent} = \frac{1}{2}\left(v_2^{\rm linear} - |l|\right). \tag{17-121}$$

Confusingly enough $v_2^{\rm bent}$ and $v_2^{\rm linear}$ are traditionally both simply called v_2. We thus have the peculiar state of affairs that two different quantities (namely $v_2^{\rm bent}$ and $v_2^{\rm linear}$) are given the same name, whereas two different names (l and k_a) are given to the same quantity. Equation (17-120) is a special case (with Λ=0) of Eq. (13-177).

The fact that the principal bending quantum number v_2 has different definitions for linear and bent triatomic molecules causes confusion concerning the value of the fundamental bending energy for a quasilinear molecule. Using linear molecule notation the fundamental bending energy is $\nu_2^{\rm linear} = E(v_1 = v_3 = 0,\ v_2^{\rm linear} = |l| = 1) - E(v_1 = v_3 = v_2^{\rm linear} = |l| = 0)$, whereas using bent molecule notation it is $\nu_2^{\rm bent} = E(v_1 = v_3 = 0,\ v_2^{\rm bent} = 1,\ K_a = 0) - E(v_1 = v_3 = v_2^{\rm bent} = K_a = 0)$. These two energies are very different from each other, and it is important to define which labeling system one is using. For an ideal linear molecule with a harmonic bending potential $\nu_2^{\rm bent} = 2\nu_2^{\rm linear}$.

The way $\nu_2^{\rm linear}$ and $\nu_2^{\rm bent}$ change as the molecule moves from being an ideal linear to an ideal bent molecule is shown in Figure 17-7 which is a quantitative rovibrational energy level correlation diagram for an isolated electronic state of a triatomic molecule. The diagram shows $J = N = 4$ energies for CH$_2$, calculated from a sequence of potential surfaces derived from the potential energy surface of $\tilde{a}\,^1A_1$ CH$_2$ with the MORBID program [see Section 15.4.7]. The $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ electronic states of CH$_2$ are degenerate as a $^1\Delta_g$ state at linearity [see Fig. 13-7 on page 374], but in the present context of showing the energy level correlation between linear and bent molecules we neglect the Renner effect [see Section 13.4.1] and treat the molecule as if it were in a $^1\Sigma$ electronic state at linearity.

The starting point for the energy level calculation is the potential energy surface for $\tilde{a}\,^1A_1$ CH$_2$ obtained by Jensen and Bunker (1988) in a least-squares fitting to experimental data.[4] This potential surface has an equilibrium bond angle ∠(HCH) of 102° (ρ_e = 78°) and a barrier to linearity of 9478 cm^{-1}; this represents an ideal bent molecule. The $J = N = 4$ rotation-vibration energies for this potential energy function are shown on the right hand side of Fig. 17-7, and they are labeled using the quantum number $v_2^{\rm bent}$. The stretching energy levels have been omitted from the figure although they were included in the calculation.

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[4] In that work the Renner effect is neglected.

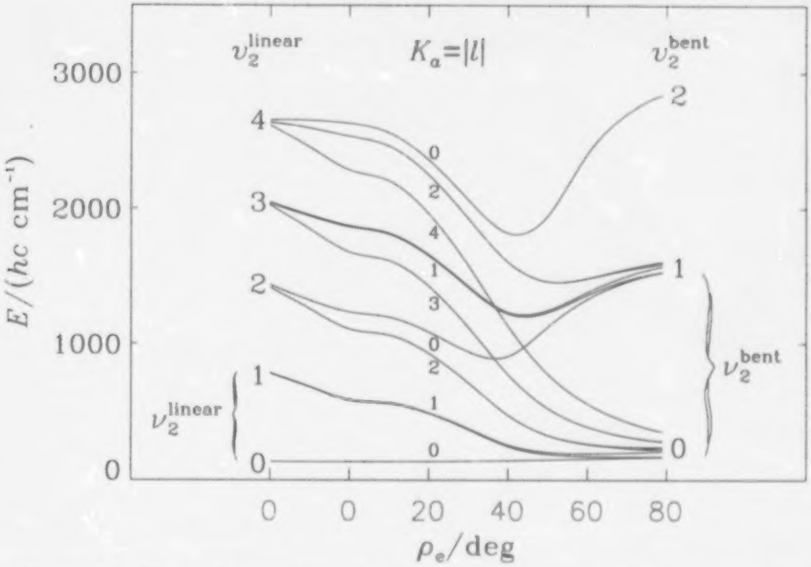

Fig. 17-7. The rovibrational energy levels of a triatomic molecule as the equilibrium structure changes from that of an ideal linear molecule (the leftmost $\rho_e=0$ point) to an ideal bent molecule on the right ($\rho_e = 78°$). The calculation is based on the parameters for $\tilde{a}\,^1A_1$ CH_2 (see text).

In the MORBID approach, the potential energy surface for an isolated electronic state is expressed as an expansion in $\cos\rho_e - \cos\rho$ and

$$y_j = 1 - \exp\left[-a_j\left(r_{j2} - r_{j2}^e\right)\right],$$

$j = 1$ or 3, where a_j is a molecular parameter and the bond lengths r_{12} and r_{32} [with equilibrium values r_{12}^e and r_{32}^e] are defined in Section 15.4.7. The parameter values for the $\tilde{a}\,^1A_1$ CH_2 potential energy used here are given in Table V of Jensen and Bunker (1988). The effect of reducing the ρ_e value to 0° is shown as we move to the left in Fig. 17-7. The results were obtained by doing the MORBID calculation eight times with $\rho_e = 70°, 60°, \ldots, 0°$ in the potential of Jensen and Bunker (1988); the $\rho_e = 0°$ result is shown above the right hand of the two $\rho_e = 0$ abscissa points. The energy levels above the left hand of the two $\rho_e = 0$ abscissa points were obtained with a change in the bending potential, still with $\rho_e = 0°$, but with the pure bending potential [i.e., the potential energy for the molecule bending with constant bond lengths $r_{12} = r_{32} = r_{12}^e$] given by

$$V_0(\rho)/(hc\ \text{cm}^{-1}) = 8000\,(1 - \cos\rho)\,. \qquad (17\text{-}122)$$

We label these energy levels using the linear molecule bending quantum number v_2^{linear}. A bending potential such as that given in Eq. (17-122) is the closest we can come to a harmonic potential using the MORBID Hamiltonian expression and it is harmonic for infinitesimal bending displacements only. It provides a good model for an ideal linear molecule. A further calculation was done with a potential half way between these two quoted $\rho_e = 0$ potentials. The eleven sets of energy levels were connected by cubic spline interpolation to produce Fig. 17-7. The zero of energy is that of the $J = v_1 = v_2 = v_3 = 0$ state at all points. We see clearly the range of usefulness of the two different bending quantum numbers and the complex rotation-bending energy level pattern that occurs when ρ_e is around 40°; this would be termed the 'quasilinear molecule region' (at $\rho_e = 40°$ the barrier to linearity is only 896 cm^{-1}). The levels can also be labeled by the rotational angular momentum quantum number $|l| = K_a$. Note that between $\rho = 50°$ and 80° the prolate-to-oblate asymmetric top energy level correlation emerges, and the splitting of the $K_a = 1$ levels is clearly seen (see also Fig. 11-1).

Although we only discuss triatomic molecules here the results can be easily extended to quasilinear chain molecules such as HCNO and C_3O_2. Yamada and Winnewisser (1976) introduce the ***quasilinearity parameter*** γ to quantify the position of a triatomic or linear chain molecule between the ideal linear and ideal bent limits. This idea has been slightly extended by Bunker and Howe (1980).

17.6 OPTICAL SELECTION RULES

A component of the dipole moment operator along a space fixed (ξ, η, ζ) direction transforms according to the representation $\Gamma^* = \Sigma_u^-$ of $\boldsymbol{D}_{\infty h}$(EM) and the representation Σ^- of $\boldsymbol{C}_{\infty v}$(EM). Thus we have the following selection rules for allowed electric dipole transitions between rovibronic states

$$\Sigma_g^+ \leftrightarrow \Sigma_u^- \qquad \text{and} \qquad \Sigma_u^+ \leftrightarrow \Sigma_g^-, \tag{17-123}$$

where the g and u labels are omitted for a $\boldsymbol{C}_{\infty v}$ molecule. These selection rules are equivalent to the standard selection rules $+ \leftrightarrow -$, s $\leftrightarrow$ s and a $\leftrightarrow$ a [see Herzberg (1991b), Eq. (II, 46) and (II, 47)].

We can rewrite Eq. (17-123) for linear molecules in totally symmetric singlet electronic states, as selection rules on the symmetry quantum number labels η and τ defined in Table 17-4 and Eqs. (17-113) and (17-114); this is in the same manner as discussed for symmetric top molecules in connection with Table 14-1. For $\boldsymbol{D}_{\infty h}$ molecules we have

$$\Delta\eta = \pm 1 \text{ and } \Delta\tau = 0, \tag{17-124}$$

and for $\boldsymbol{C}_{\infty v}$ molecules

$$\Delta\tau = \pm 1. \tag{17-125}$$

The calculation of intensities for linear molecules can be carried in much the same way as described for nonlinear molecules in Chapter 14, at least as long as we neglect the effects of electron spin. If we consider electron spin effects, it will be appropriate to use a Hund's case (a) basis, and not the Hund's case (b) basis employed in Chapter 14 for nonlinear molecules. However, Eqs. (14-33) and (14-43) are valid for linear molecules.

Pure rotation transitions are forbidden for centrosymmetric molecules (see page 456), and hence they are forbidden for linear molecules of $\boldsymbol{D}_{\infty \mathrm{h}}$ symmetry. Rotation-vibration transitions are not necessarily forbidden for a linear molecule with symmetry $\boldsymbol{D}_{\infty \mathrm{h}}$, and to determine the selection rules for transitions within one electronic state e'' say, we use the symmetry results that

$$\Gamma\left(\mu_x(e'',e''),\mu_y(e'',e'')\right) = \Pi_{\mathrm{u}} \tag{17-126}$$

and

$$\Gamma\left(\mu_z(e'',e'')\right) = \Sigma_{\mathrm{u}}{}^{+}, \tag{17-127}$$

where the Cartesian components $\mu_\alpha(e'',e'')$, $\alpha = x$, y, z, of the electronic transition moment function are defined in Eq. (14-38). For a linear molecule with $\boldsymbol{C}_{\infty \mathrm{v}}$ symmetry, the subscripts 'u' in Eqs. (17-126) and (17-127) are omitted. Thus, in order for the vibronic matrix elements

$$\left\langle \Phi_{\mathrm{vib}}^{(V',L')} \left| \mu_{\mathrm{m}}^{(1,\sigma')}(e',e'') \right| \Phi_{\mathrm{vib}}^{(V'',L'')} \right\rangle$$

in Eq. (14-44) to be nonvanishing for a $\boldsymbol{D}_{\infty \mathrm{h}}$ molecule, we have from Eq. (14-40) that one of the equations

$$\Gamma''_{\mathrm{vib}} \otimes \Gamma'_{\mathrm{vib}} \supset \Pi_{\mathrm{u}} \tag{17-128}$$

or

$$\Gamma''_{\mathrm{vib}} \otimes \Gamma'_{\mathrm{vib}} \supset \Sigma_{\mathrm{u}}{}^{+} \tag{17-129}$$

must be satisfied [where we omit the 'u' subscripts for a molecule of $\boldsymbol{C}_{\infty \mathrm{v}}$ symmetry]. For a Σ electronic state with $\Lambda = 0$, it follows from Eqs. (14-14) and (17-74) together with the condition $\sigma' = k' - k''$ discussed after Eq. (14-34), that if Eq. (17-128) is fulfilled for the vibronic matrix element given above, then the two vibrational functions $\Phi_{\mathrm{vib}}^{(V',L')}$ and $\Phi_{\mathrm{vib}}^{(V'',L'')}$ satisify $\Delta l = \pm 1$, whereas if Eq. (17-129) is fulfilled, the two functions satisfy $\Delta l = 0$.

17.7 ELECTRONIC g/u MIXING

For a homonuclear diatomic molecule, interactions between the rotational levels of vibronic states having g and u symmetry can occur as a result of the effect of the nuclear spin part of the molecular Hamiltonian ($\hat{H}_{\mathrm{ns}}$ in Table 7-1). Such so-called g/u mixing is likely to be observed if a g and a u vibronic state are close in energy. If a g and a u electronic state share the same dissociation limit, the conditions for g/u mixing will be fulfilled in the energy region immediately below this limit. This type of mixing was observed for the first time in the I_2 molecule [Pique, Hartmann, Bacis, Churassy, and Koffend (1984)]. It has also been observed in Cs_2 [Weickenmeier, Diemer, Demtröder, and Broyer (1986)] and, fairly recently, in H_2^+ [see Moss (1993) and references therein]. We will explain the situation for H_2^+ in detail.

For the H_2^+ molecular ion all of its electronic states are doublet states with $S = 1/2$; hence we use N as the quantum number associated with the rovibronic angular momentum and J as the quantum number associated with the sum of the rovibronic angular momentum and the electron spin.

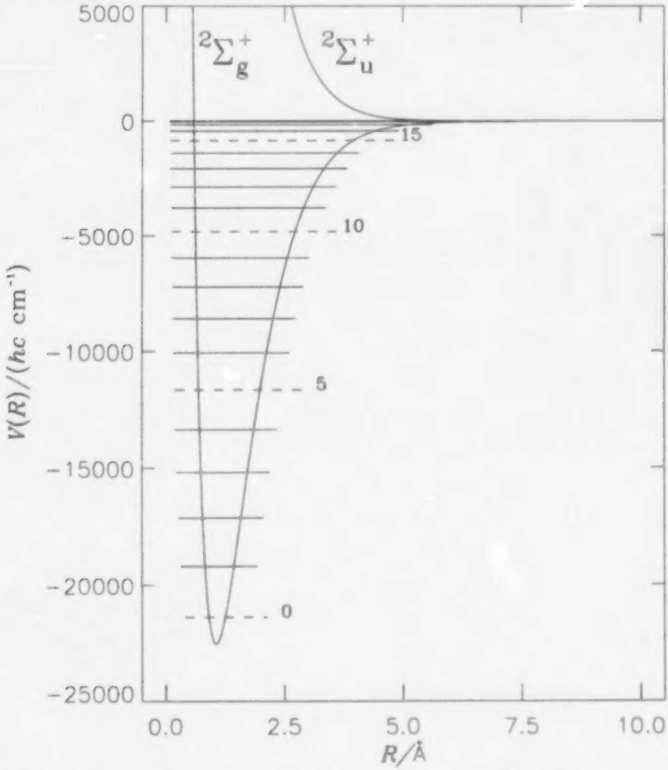

Fig. 17-8. The potential energy curves for the $\tilde{X}\,^2\Sigma_g^+$ and $\tilde{A}\,^2\Sigma_u^+$ electronic states of H_2^+ [Moss (1998)]. There are 20 bound vibrational states in the $\tilde{X}$ electronic state, and the energies of the v = 0, 5, 10, and 15 states are drawn as dashed lines.

The $\tilde{X}\,^2\Sigma_g^+$ electronic ground state and $\tilde{A}\,^2\Sigma_u^+$ first excited electronic state of H_2^+ have the same dissociation limit. Figure 17-8 shows the potential energy curves for the $\tilde{X}$ and $\tilde{A}$ electronic states [Moss (1998)]. On the scale of the figure, the $\tilde{A}\,^2\Sigma_u^+$ state appears to be purely repulsive, but in Fig. 17-9 we show an enlargement of the energy region very close to dissociation, and it is seen that the $\tilde{A}$ state potential curve has a very shallow minimum at a large value of the internuclear distance. There is observable g/u mixing between the rotational levels of the $v = 0$ level of the $\tilde{A}$ state and the $v = 18$ and 19 levels of the $\tilde{X}$ state, and we now explain the symmetry conditions that make this possible.

The vibronic levels of the $\tilde{X}\,^2\Sigma_g^+$ electronic state all have Σ_g^+ symmetry, and the vibronic levels of the $\tilde{A}\,^2\Sigma_u^+$ electronic state all have Σ_u^+ symmetry. From Fig. 17-6 we can obtain the symmetries of the individual rovibronic states (rotational levels) of each of these states. For the $\tilde{X}$ state the rovibronic symmetry is Σ_g^+ (+s) for N even and Σ_g^- (−a) for N odd. The rovibronic states associated with the $\tilde{A}$ electronic state have Σ_u^+ (+a) symmetry for N even and Σ_u^- (−s) symmetry for N odd. Rovibronic interactions cannot mix the levels of these two electronic states because of their g/u distinction. However, nuclear spin effects can.

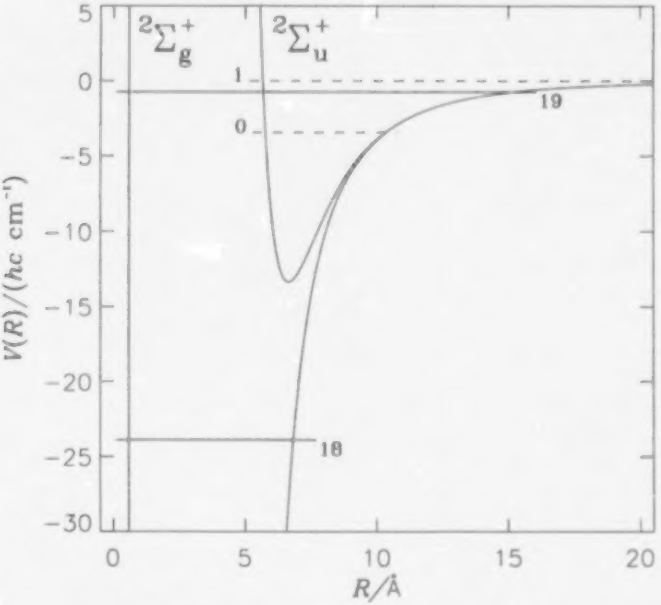

Fig. 17-9. The potential energy curves for the $\tilde{X}\,^2\Sigma_g^+$ and $\tilde{A}\,^2\Sigma_u^+$ electronic states of H_2^+ close to dissociation [Moss (1998)]. The $\tilde{A}\,^2\Sigma_u^+$ potential curve has a very shallow minimum and the theoretical calculation of Moss (1998) predicts that it supports two bound vibrational states. The energies of these states are shown as dashed lines and labeled by their respective v values. The $v = 1$ energy lies 0.00023 cm^{-1} below the dissociation limit and it is dubious whether it exists in the real molecule. The energies of the $v = 18$ and 19 states of the $\tilde{X}\,^2\Sigma_g^+$ electronic state are also indicated.

For H_2^+ there is one nuclear spin function with total spin $I = 0$ [the para function] having $\Sigma_u{}^+$ (+a) symmetry, and three functions with $I = 1$ [the ortho functions] each having $\Sigma_g{}^+$ (+s) symmetry. The internal (rovibronic nuclear-spin) wavefunction can only have the symmetries $\Gamma_{\rm MS}^+ = \Sigma_u{}^+$ (+a) and $\Gamma_{\rm MS}^- = \Sigma_g{}^-$ (−a) from the Pauli exclusion principle. Thus in the $\tilde{X}\,{}^2\Sigma_g{}^+$ electronic state the rovibronic states with N even are para states with $\Gamma_{\rm int} = \Sigma_u{}^+$, and rovibronic states with N odd are ortho states with $\Gamma_{\rm int} = \Sigma_g{}^-$. On the other hand in the $\tilde{A}\,{}^2\Sigma_u{}^+$ electronic state, the rovibronic states with N even are ortho states with $\Gamma_{\rm int} = \Sigma_u{}^+$, and rovibronic states with N odd are para states with $\Gamma_{\rm int} = \Sigma_g{}^-$. Thus the MS group symmetry allows an interaction between $\tilde{X}\,{}^2\Sigma_g{}^+$ and $\tilde{A}\,{}^2\Sigma_u{}^+$ internal wavefunctions with the same N value. The interaction couples states of g rovibronic symmetry with states of u rovibronic symmetry; it is a g/u mixing . The g/u mixing is simultaneously an ortho/para mixing as already mentioned in Section 14.1.16.

In terms of the MS group symmetry, there is obviously nothing particularly mysterious about g/u mixing. However, since it involves ortho-para interaction it is caused by the operator $\hat{H}_{\rm ns}$ in Table 7-1, and consequently it is a very small effect which can only be observed when two vibronic states of g and u symmetry are close in energy. The gross, easily observable features of centrosymmetric molecule spectra can be interpreted in terms of g/u symmetry, and only small nuclear spin effects cause this symmetry to break down. In the case of H_2^+ discussed above, Moss (1993) has attributed the g/u mixing to the *Fermi contact interaction operator*

$$\begin{aligned}\hat{H}_{\rm FCI} &= \frac{8\pi}{3}\,\frac{g\,g_{\rm N}\,\mu_{\rm N}\,\mu_{\rm B}}{4\pi\epsilon_0 c^2}\,\left[\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{I}}_1\,\delta\,(\boldsymbol{r}_{\rm e}-\boldsymbol{R}_1)+\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{I}}_2\,\delta\,(\boldsymbol{r}_{\rm e}-\boldsymbol{R}_2)\right]\\ &= \frac{8\pi}{6}\,\frac{g\,g_{\rm N}\,\mu_{\rm N}\,\mu_{\rm B}}{4\pi\epsilon_0 c^2}\,\hat{\boldsymbol{S}}\cdot\left[\hat{\boldsymbol{I}}_+\,\delta_+ + \hat{\boldsymbol{I}}_-\,\delta_-\right],\end{aligned} \qquad (17\text{-}130)$$

where $\boldsymbol{r}_{\rm e}$ is the position vector of the electron, $\boldsymbol{R}_\alpha$, $\alpha = 1$ or 2, is the position vector of nucleus α,

$$\hat{\boldsymbol{I}}_\pm = \hat{\boldsymbol{I}}_1 \pm \hat{\boldsymbol{I}}_2, \qquad (17\text{-}131)$$

and

$$\delta_\pm = \delta\,(\boldsymbol{r}_{\rm e}-\boldsymbol{R}_1) \pm \delta\,(\boldsymbol{r}_{\rm e}-\boldsymbol{R}_2)\,. \qquad (17\text{-}132)$$

The Fermi-contact-type interaction described by the operator $\hat{H}_{\rm FCI}$ is that between the nuclei and the electron; the analogous interaction between electrons is described by the last term in Eq. (7-22). It follows from the discussion given in connection with Eq. (4-11) that both $\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{I}}_+\,\delta_+$ and $\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{I}}_-\,\delta_-$ on the right hand side of Eq. (17-130) are invariant under the MS group operation (12)*. The first term is also invariant under the point group operation i and conserves g/u symmetry, but the second term is antisymmetric under i and is responsible for the g/u mixing [see Fig. 2 of Moss (1993)].

These g/u interactions in H_2^+ causes unexpectedly large hyperfine splittings in the transitions between rotational levels belonging to the $\tilde{A}\,{}^2\Sigma_u{}^+$, $v = 0$

vibronic state and rotational levels belonging to the $\tilde{X}\,^2\Sigma_g{}^+$, $v = 18$ and 19 vibronic states. The levels involved are very close to the dissociation limit [see Fig. 17-9], and the transition frequencies fall in the microwave region. For further details, see Moss (1993) and the references to the experimental work in the Bibliographical Notes. Such electronic g/u interactions make it possible for pure rotation (ortho-para) transitions to be observed within the highest vibrational levels of the $\tilde{X}$ state, and within the $v = 0$ level of the $\tilde{A}$ state; they have not yet been seen.

As mentioned above, electronic g/u mixing has also been observed in transitions of the I_2 molecule involving levels from 28 cm^{-1} to 0.5 cm^{-1} below the $^2P_{1/2} + {}^2P_{3/2}$ dissociation limit [Pique, Hartmann, Bacis, Churassy, and Koffend (1984); Pique, Hartmann, Churassy, and Bacis (1986a)]. The I_2 electronic states studied are singlet states, and so the g/u mixing is due to terms in $\hat{H}_{ns}$ that do not involve the electron spins, as it is for electronic g/u mixing in the H_2 molecule (see the Bibliographical Notes concerning ortho-para interactions at the end of Chapter 14). See the Bibliographical Notes of the present Chapter for references to relevant theoretical work on I_2.

BIBLIOGRAPHICAL NOTES

Bunker (1974). Within the Born-Oppenheimer approximation homopolar isotopically unsymmetrical diatomic ions, for example HD^+ and $^{35}Cl^{37}Cl^+$, have $\boldsymbol{D}_{\infty h}$ symmetry and a nonvanishing dipole moment; this seems paradoxical. The apparent group theoretical paradox is reconciled in this paper by treating carefully the transformation properties of the dipole moment operator under the effect of the operation of permuting the two nuclei. Although the two nuclei are not identical the Hamiltonian within the Born-Oppenheimer approximation is invariant to their exchange and does have $\boldsymbol{D}_{\infty h}$ symmetry.

Electronic g/u mixing in H_2^+

Moss (1993). This paper describes the theory necessary to explain the experimental results reported in the following series of references:

Carrington, McNab, Montgomerie, and Kennedy (1989).
Carrington, McNab, and Montgomerie (1989).
Carrington, McNab, Montgomerie, and Kennedy (1991).
Carrington, Leach, Moss, Steimle, Viant, and West (1993).
Carrington, Leach, Marr, Moss, Pyne, and Steimle (1993).

Electronic g/u mixing in I_2

Pique, Hartmann, Bacis, Churassy, and Koffend (1984). First reported experimental observation of g/u mixing.

Pique, Hartmann, Churassy, and Bacis (1986a). Experimental paper. All the following papers are theoretical.

Pique, Hartmann, Churassy, and Bacis (1986b).
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Vigué, Broyer, and Lehmann (1981).

18

Electron Spin Double Groups

When a molecule has an odd number of electrons with strong spin–orbit coupling the rovibronic wavefunctions involve half integral angular momentum quantum numbers. The symmetry transformation of such wavefunctions presents a problem, as we show using the three dimensional rotation group $\boldsymbol{K}$. *To get around this problem a special symmetry operation (that we call R) is introduced, and this operation involves the rotation of the molecule through 2π radians; it is considered to be distinct from the identity operation. The operation R, which is unitary, can be taken to be identical to* $\hat{\theta}^2$, *the square of the anti-unitary time reversal symmetry operation* $\hat{\theta}$ *introduced in Section 7.4. The spin double group of an MS group is obtained by including R, and the product of it with all the elements of the MS group, in the group. We determine the character tables of the spin double groups* $C_{2v}(M)^2$ *and* $C_{3v}(M)^2$ *as examples. It is shown that for a nonrigid molecule the character table of the spin double group of the MS group can depend on which part of the molecule the electron spin is 'tied' to by the spin–orbit coupling. Several examples of character tables of spin double groups of MS groups are given in the Appendix of this chapter.*

18.1 SPIN DOUBLE GROUPS AND THE OPERATION R

Let us consider the implication of taking the elements of the matrices in the representations $D^{(j)}$ of $\boldsymbol{K}$, when j is half-integral to be as given when j is integral by combining Eqs. (11-13) and (11-15). The character of this $D^{(j)}$ under an operation involving a rotation through an angle ε is given by [see Tinkham (1964), page 109; or Hamermesh (1964), page 355; or Wigner (1959), Eq. (15-28)]

$$\chi^{(j)}(\varepsilon) = \frac{\sin[(2j+1)\varepsilon/2]}{\sin(\varepsilon/2)}. \tag{18-1}$$

The character for a rotation through an angle $\varepsilon + 2\pi$ radians is thus given by

$$\chi^{(j)}(\varepsilon + 2\pi) = \frac{\sin[(2j+1)\varepsilon/2 + (2j+1)\pi]}{\sin[(\varepsilon/2) + \pi]}. \tag{18-2}$$

For j integral or half-integral we can deduce from Eq. (18-2) that

$$\chi^{(j)}(\varepsilon + 2\pi) = (-1)^{2j}\chi^{(j)}(\varepsilon) \tag{18-3}$$

and also that

$$\chi^{(j)}(\varepsilon + 4\pi) = \chi^{(j)}(\varepsilon). \tag{18-4}$$

From Eq. (18-3) we see that if j is half-integral then

$$\chi^{(j)}(\varepsilon + 2\pi) = -\chi^{(j)}(\varepsilon). \tag{18-5}$$

Since a rotation through 2π is equivalent to no rotation at all the character in this $D^{(j)}$, when j is half-integral, under each operation in $\boldsymbol{K}$ is ambiguous with regard to its sign; the character is ***double valued***. It would appear that we cannot set up representations for half-integral j using these $D^{(j)}$ since we do not have $D[P_1]D[P_2] = D[P_{12}]$ but only[1] $D[P_1]D[P_2] = \pm D[P_{12}]$ [see Eq. (6-172)]. Following Bethe (1929) this situation is dealt with by introducing the operation R which is a rotation through 2π but which is not considered to be the identity.

In this way we double the number of operations in $\boldsymbol{K}$ and we call the group $\boldsymbol{K}^2$, ***the spin double group of the three-dimensional rotation group***. This is very similar to the way the extended molecular symmetry group for dimethylacetylene is introduced on page 520. In the spin double group the rotation through an angle $\varepsilon + 2\pi$ is considered distinct from a rotation through ε and Eq. (18-5) no longer results in a sign ambiguity since ε and $\varepsilon + 2\pi$ are considered as different operations. The character of a representation matrix in $D^{(j)}$ having j half-integral will have opposite sign under a rotation through $\varepsilon + 2\pi$ from its value under a rotation through ε; this representation is a single valued representation (i.e., a true representation) of the spin double group $\boldsymbol{K}^2$ or a (so-called) double valued representation of the group $\boldsymbol{K}$. A representation $D^{(j)}$ for which j is integral will have the same character under a rotation through ε as under a rotation through $\varepsilon + 2\pi$ and constitutes a single valued representation of the group $\boldsymbol{K}$. In the group $\boldsymbol{K}^2$ a rotation through $\varepsilon + 4\pi$ is equivalent to a rotation of ε about the axis and R^2 is the identity.

The ***spin double group*** of an MS group is obtained by doubling the number of elements in the MS group in the same way that we double the number of elements in $\boldsymbol{K}$ to obtain $\boldsymbol{K}^2$. To do this we must include the operation R, which is a rotation through 2π, in the MS group. Thus for each permutation or permutation–inversion operation O that occurs in an MS group, we add the operation RO which is defined as causing the same permutation (or permutation–inversion) of the nuclei and electrons as O but which causes a rotation of 2π in addition to the rotation caused by O. The effect of RO on the spatial coordinates of the nuclei and electrons is the same as the effect of O.

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[1] However, see the Bibliographical Notes.

Let us consider the equivalent rotations (see Table 12-1) of permutation or permutation–inversion elements O, of the operation R, and of the combined operations RO. In the ordinary MS group, in which a rotation through 2π radians is the identity, we can write the effect of the equivalent rotation of each MS group element using the following equations

$$R_z{}^{\beta}(\theta,\phi,\chi) = (\theta,\phi,\chi+\beta) \tag{18-6}$$

and

$$R_\alpha{}^{\pi}(\theta,\phi,\chi) = (\pi-\theta,\phi+\pi,2\pi-2\alpha-\chi), \tag{18-7}$$

where $0 \le \theta \le \pi, 0 \le \phi \le 2\pi$, and $0 \le \chi \le 2\pi$. In a spin double group of an MS group the rotation through 2π radians is not the identity. We can allow for this by taking the ranges of the Euler angles as $0 \le \theta \le \pi, 0 \le \phi \le 4\pi$, and $0 \le \chi \le 4\pi$ (where ϕ and χ are mod 4π), and by taking

$$\begin{aligned} R^0(\theta,\phi,\chi) &= (\theta,\phi,\chi) \text{ or } (\theta,\phi+2\pi,\chi+2\pi),\\ R_z{}^{\beta}(\theta,\phi,\chi) &= (\theta,\phi,\chi+\beta) \text{ or } (\theta,\phi+2\pi,\chi+2\pi+\beta),\\ R_\alpha{}^{\pi}(\theta,\phi,\chi) &= (\pi-\theta,\phi+\pi,2\pi-2\alpha-\chi) \text{ or } (\pi-\theta,\phi+3\pi,4\pi-2\alpha-\chi); \end{aligned} \tag{18-8}$$

and

$$\begin{aligned} R^{2\pi}(\theta,\phi,\chi) &= (\theta,\phi,\chi+2\pi) \text{ or } (\theta,\phi+2\pi,\chi),\\ R^{2\pi}R_z{}^{\beta}(\theta,\phi,\chi) &= (\theta,\phi,\chi+2\pi+\beta) \text{ or } (\theta,\phi+2\pi,\chi+\beta),\\ R^{2\pi}R_\alpha{}^{\pi}(\theta,\phi,\chi) &= (\pi-\theta,\phi+\pi,4\pi-2\alpha-\chi) \text{ or } (\pi-\theta,\phi+3\pi,2\pi-2\alpha-\chi). \end{aligned} \tag{18-9}$$

In this treatment there are two Euler angle transformations for each equivalent rotation but this does not present any difficulty in applications.

All the elements of the spin double group are unitary and, therefore, the group has classes and representations in the normal way.[2] From the above discussion it might appear that the MS group is a subgroup of the spin double group, but this is not so. In the spin double group permutations P and permutation-inversions P^* can multiply together to give elements that involve R. For example, $(12)(12) = R$ in $\boldsymbol{C}_{2v}(\mathrm{M})^2$ (see Table 18-2), and $(132)(132) = R(123)$ in $\boldsymbol{C}_{3v}(\mathrm{M})^2$ (see Table 18-7). Thus even though $\{E, R\}$ is an invariant subgroup of the spin double group, since $R^2 = E$ and R commutes with all elements of the MS group, the spin double group is *not* the direct or semidirect product of the MS group and $\{E, R\}$ since the MS group is not a subgroup of the spin double group. Therefore the ideas of Sections 5.7, 5.8.2, and 6.3.1, and Appendix 16-1, cannot be used to determine the characters of the irreducible representations, or to determine appropriately symmetrized basis functions. In order to determine the characters of the irreducible representations we use Eqs. (5-68) and (5-69).

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[2] In Section 7.4 we discuss the problem that occurs if we try to define representations of a group that contains anti-unitary operations such as the time reversal operation $\hat{\theta}$.

In a spin double group the representations having character +1 under R are single valued representations of the MS group, and those having character −1 under R are double valued representations of the MS group. They are true representations of the spin double group. In Appendix 18-1 the character tables of the spin double groups of several MS groups are given. As in Herzberg (1991b) these character tables are arranged so that the upper left 'box' is the character table of the MS group. States having half-integral angular momentum quantum numbers will transform as the double valued irreducible representations of the MS group, and because of Kramers' theorem [Kramers (1930)] they will be doubly degenerate. The subscript notation $(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots)$ for the double valued irreducible representations of the MS group in the spin double groups is (where possible) that adopted by Herzberg (1991b) and is obtained from the lowest j value of the representation $D^{(j)}$ of $\boldsymbol{K}(\mathrm{mol})^2$ with which the irreducible representation correlates (see Table B-2). To show how the character tables of the spin double groups of the MS groups are determined we consider the groups $\boldsymbol{C}_{2v}(\mathrm{M})^2$ and $\boldsymbol{C}_{3v}(\mathrm{M})^2$ as examples below.

Dr. J. K. G. Watson has shown us that the square of the time reversal symmetry operation $\hat{\theta}^2$ (see Section 7.4) has all the properties of the operation R discussed here, and indeed[3] we can consider R to be $\hat{\theta}^2$. From Eq. (7-51) we see that for a molecule having an odd number of particles with half-integral spin the wavefunction is changed in sign by $\hat{\theta}^2$, and we further see that $\hat{\theta}^4$ $(=R^2)$ is the identity for all molecules. Hence, taking $R = \hat{\theta}^2$, the spin double group of an MS group is the unitary subgroup of the unitary-antiunitary group obtained by combining the MS group with the group $\{E, \hat{\theta}, \hat{\theta}^2, \hat{\theta}^3\}$.

18.2 THE SPIN DOUBLE GROUP OF C_{2v}(M)

The operations of the $\boldsymbol{C}_{2v}(\mathrm{M})^2$ group are

$$E, (12), E^*, (12)^*, R, R(12), RE^*, \text{ and } R(12)^*, \qquad (18\text{-}10)$$

and the equivalent rotations of these elements for the H$_2$O molecule are (see Fig. 12-7)

$$R^0, R_b^\pi, R_c^\pi, R_a^\pi, R^{2\pi}, R_b^{3\pi}, R_c^{3\pi}, \text{ and } R_a^{3\pi}, \qquad (18\text{-}11)$$

respectively. The Euler angle transformations (using the I^r representation) are given in Table 18-1 [only one of the two possibilities from Eqs. (18-8) and (18-9) are given]. The equivalent rotations in Eq. (18-11) (or the results in Table 18-1) are required in the calculation of the multiplication table of the group elements.

For example, as far as the effect of the elements on the coordinates of the nuclei and electrons in space is concerned we can write the product E^* times $(12)^*$ as

$$E^*(12)^* = (12) \text{ or } R(12), \qquad (18\text{-}12)$$

---

[3] **Using the principle that if it looks like a duck, flies like a duck, and quacks like a duck then it is a duck.**

Table 18-1

Transformation properties of the Euler angles of H_2O^a for the elements of the group $C_{2v}(M)^2$

E	(12)	E^*	$(12)^*$	R	$R(12)$	RE^*	$R(12)^*$
θ	$\pi-\theta$	$\pi-\theta$	θ	θ	$\pi-\theta$	$\pi-\theta$	θ
ϕ	$\phi+\pi$	$\phi+\pi$	ϕ	ϕ	$\phi+\pi$	$\phi+\pi$	ϕ
χ	$2\pi-\chi$	$\pi-\chi$	$\chi+\pi$	$\chi+2\pi$	$4\pi-\chi$	$3\pi-\chi$	$\chi+3\pi$

[a] A I^r convention is used; ϕ and χ are mod 4π and $0 \leq \theta \leq \pi$.

but the Euler angle transformations distinguish between these two possibilities. We can write

$$\begin{aligned} E^*(12)^*(\theta,\phi,\chi) = E^*(\theta',\phi',\chi') &= (\pi-\theta',\phi'+\pi,\pi-\chi') \\ &= (\pi-\theta,\phi+\pi,-\chi), \end{aligned} \tag{18-13}$$

where

$$(12)^*(\theta,\phi,\chi) = (\theta',\phi',\chi') = (\theta,\phi,\chi+\pi). \tag{18-14}$$

From Eq. (18-13) and Table (18-1) we see that

$$E^*(12)^* = R(12) \tag{18-15}$$

since $(4\pi-\chi)$ and $-\chi$ are equivalent (χ is defined mod 4π in the spin double group).

Table 18-2

Multiplication table for the elements of $C_{2v}(M)^2$ obtained using the Euler angle transformations given in Table 18-1

	E	(12)	E^*	$(12)^*$	R	$R(12)$	RE^*	$R(12)^*$
E :	E	(12)	E^*	$(12)^*$	R	$R(12)$	RE^*	$R(12)^*$
(12) :	(12)	R	$R(12)^*$	E^*	$R(12)$	E	$(12)^*$	RE^*
E^* :	E^*	$(12)^*$	R	$R(12)$	RE^*	$R(12)^*$	E	(12)
$(12)^*$:	$(12)^*$	RE^*	(12)	R	$R(12)^*$	E^*	$R(12)$	E
R :	R	$R(12)$	RE^*	$R(12)^*$	E	(12)	E^*	$(12)^*$
$R(12)$:	$R(12)$	E	$(12)^*$	RE^*	(12)	R	$R(12)^*$	E^*
RE^* :	RE^*	$R(12)^*$	E	(12)	E^*	$(12)^*$	R	$R(12)$
$R(12)^*$:	$R(12)^*$	E^*	$R(12)$	E	$(12)^*$	RE^*	(12)	R

The multiplication table[4] of the elements of the $C_{2v}(M)^2$ group, derived by considering equations such as the preceding, is shown in Table 18-2. From the results in Table 18-2 we can determine the class structure of the elements of the $C_{2v}(M)^2$ group [see Eq. (5-49)], and this is given in Table 18-3. We are now in a position to use Eqs. (5-68) and (5-69) to determine the characters of the irreducible representations of $C_{2v}(M)^2$. Using Eq. (5-68) the following class products can be determined from the results in Tables 12-5 and 18-3:

$$C_5^2 = C_1 \tag{18-16}$$

$$C_2^2 = 2C_1 + 2C_5, \tag{18-17}$$

$$C_3^2 = 2C_1 + 2C_5, \tag{18-18}$$

$$C_2C_3 = 2C_4. \tag{18-19}$$

For a two-dimensional representation of $C_{2v}(M)^2$ the character under E is 2, i.e., $\chi[E] = \chi_1 = 2$, and the preceding equations, in conjunction with Eq. (5-69), lead to the following relationships among the characters of a two-dimensional representation:

$$\chi_5^2 = 4, \tag{18-20}$$

$$\chi_2^2 = 2 + \chi_5, \tag{18-21}$$

$$\chi_3^2 = 2 + \chi_5, \tag{18-22}$$

$$\chi_2\chi_3 = 2\chi_4. \tag{18-23}$$

The characters for the two-dimensional representations of $C_{2v}(M)^2$ that follow from these equations are given in Table 18-4. The two-dimensional representations thus have characters as given in Table 18-5. From Eq. (5-46) we see that the representation Γ_5 in Table 18-5 is irreducible but that Γ_1 to Γ_4 are reducible. The reduction of Γ_1 to Γ_4 is obvious (they are each twice an irreducible representation) and the character table (see Table 18-19) follows.

Table 18-3

The class structure of the group $C_{2v}(M)^2$

C_1	C_2	C_3	C_4	C_5
E	(12) $R(12)$	E^* RE^*	$(12)^*$ $R(12)^*$	R

---

[4] In a spin double group E^*P and PE^* are not necessarily equal and $(E^*)^2 = R$.

Table 18-4

The determination of the characters of the two-dimensional representations of $C_{2v}(M)^2$ from Eqs. (18-20)–(18-23).

Equation	Character	Value				
	χ_1	+2				
Eq. (18-20)	χ_5	+2		+2		
Eq. (18-21)	χ_2	+2		−2	0	
Eq. (18-22)	χ_3	+2	−2	+2	−2	0
Eq. (18-23)	χ_4	+2	−2	−2	+2	0

Table 18-5

Characters of two-dimensional representations of $C_{2v}(M)^2$ obtained from Table 18-4

	C_1	C_2	C_3	C_4	C_5
Γ_1:	2	2	2	2	2
Γ_2:	2	2	−2	−2	2
Γ_3:	2	−2	2	−2	2
Γ_4:	2	−2	−2	2	2
Γ_5:	2	0	0	0	−2

18.2.1 An example: NF_2

As an example of the use of the $C_{2v}(M)^2$ spin double group let us consider the NF_2 molecule in an excited ${}^2B_1$ electronic state and determine the symmetry labels in the Hund's case (a) and (b) limits.

We consider levels of NF_2 in which the vibrational state is totally symmetric. In the case (b) limit the electron spin wavefunctions are totally symmetric and the rovibronic species Γ_{rve} are obtained by multiplying the rotational species Γ_{rot} for the levels $N_{K_a K_c}$ (given in Table 12-8 with $N = J$) by the vibronic species B_1. Since $S = \frac{1}{2}$ we have $J = N \pm \frac{1}{2}$, and the rovibronic–electron spin species Γ_{rves} are as given down the right hand side in Fig. 18-1. In the

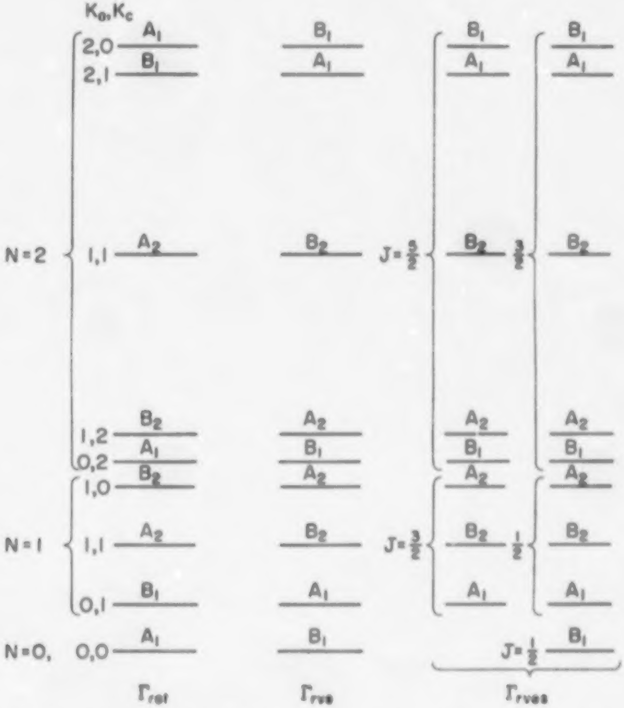


Fig. 18-1. The symmetry labels Γ_{rves} for the rovibronic–electron spin energy levels of NF_2 in a $^2B_1$ vibronic state using Hund's case (b) electron spin functions.

case (a) limit (see Section 12.5.3) the electron spin species Γ_{espin} is obtained by reducing $D^{(S)} = D^{(1/2)}$ of $\boldsymbol{K}(\mathrm{mol})^2$ onto the double group $\boldsymbol{C}_{2v}(\mathrm{M})^2$ and this gives $\Gamma_{espin} = E_{1/2}$. Multiplying by the electron orbital species B_1 we obtain the spin–orbit species $\Gamma_{eso} = E_{1/2}$. The rotational species Γ_{rot} cannot be obtained from Table 12-8 since now we have to classify the functions $J_{P_aP_c}$ where J is half-integral; in case (a), for a molecule with an odd number of electrons, S and hence J, are always half-integral. For NF_2 we can use the correlation table for $\boldsymbol{K}(\mathrm{mol})^2 \to \boldsymbol{C}_{2v}(\mathrm{M})^2$ to obtain the following results for the species of the rotational wavefunctions as a function of J:

$$\Gamma_{rot}\left(J = \frac{1}{2}\right) = E_{1/2}, \qquad \Gamma_{rot}\left(J = \frac{3}{2}\right) = 2E_{1/2}, \qquad (18\text{-}24)$$

and

$$\Gamma_{rot}\left(J = \frac{5}{2}\right) = 3E_{1/2}.$$

Using the result that in $\mathbf{C}_{2v}(M)^2$

$$E_{1/2} \otimes E_{1/2} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \tag{18-25}$$

we obtain the rovibronic–electron spin species Γ_{rves} as given down the right hand side in Fig. 18-2. For a given value of J we obtain, as we must, the same species as obtained using the case (b) basis. To classify the individual $J_{P_a P_c}$ functions we must determine the transformation properties of the symmetric top basis functions with half-integral J in the group $\mathbf{C}_{2v}(M)^2$ and this general problem is discussed in Section 18.5.

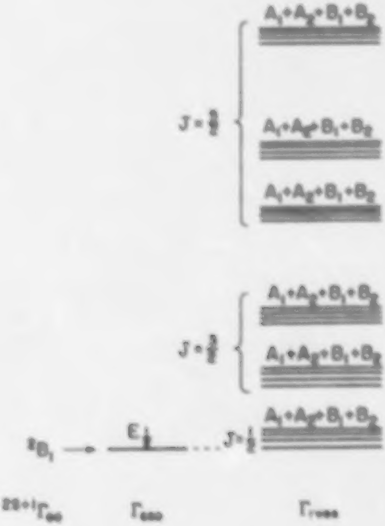


Fig. 18-2. The symmetry labels Γ_{rves} for the rovibronic–electron spin energy levels of NF_2 in a $^2B_1$ electronic state (and an A_1 vibrational state) using Hund's case (a) electron spin functions.

18.3 THE SPIN DOUBLE GROUP OF $\mathbf{C}_{3v}(M)$

The spin double group of the MS group of CH_3F is called $\mathbf{C}_{3v}(M)^2$ and it consists of the following 12 elements (see Table 18-20):

$$\{E, (123), (132), (12)^*, (23)^*, (13)^*, R, R(123), R(132), R(12)^*, R(23)^*, R(13)^*\}. \tag{18-26}$$

The equivalent rotations of these 12 elements are, respectively,

$$\begin{gathered} R^0, R_z^{2\pi/3}, R_z^{4\pi/3}, R_{\pi/6}^{\pi}, R_{\pi/2}^{\pi}, R_{5\pi/6}^{\pi}, R^{2\pi}, R^{2\pi} R_z^{2\pi/3}, \\ R^{2\pi} R_z^{4\pi/3}, R^{2\pi} R_{\pi/6}^{\pi}, R^{2\pi} R_{\pi/2}^{\pi}, R^{2\pi} R_{5\pi/6}^{\pi}. \end{gathered} \tag{18-27}$$

For convenience in the character tables of Appendix 18-1 we write the equivalent rotations $R^{2\pi} R_z{}^{\beta}$ and $R^{2\pi} R_\alpha{}^{\pi}$ as $R_z^{\beta+2\pi}$ and $R_\alpha^{3\pi}$ respectively.

Table 18-6

The definition of the effect of each operation of the $C_{3v}(M)^2$ group on the Euler angles[a]

E	(123)	(132)	$(12)^*$	$(23)^*$	$(13)^*$
θ	θ	θ	$\pi-\theta$	$\pi-\theta$	$\pi-\theta$
ϕ	ϕ	ϕ	$\phi+\pi$	$\phi+\pi$	$\phi+\pi$
χ	$\chi+2\pi/3$	$\chi+4\pi/3$	$5\pi/3-\chi$	$\pi-\chi$	$\pi/3-\chi$
R	$R(123)$	$R(132)$	$R(12)^*$	$R(23)^*$	$R(13)^*$
θ	θ	θ	$\pi-\theta$	$\pi-\theta$	$\pi-\theta$
ϕ	ϕ	ϕ	$\phi+\pi$	$\phi+\pi$	$\phi+\pi$
$\chi+2\pi$	$\chi+8\pi/3$	$\chi+10\pi/3$	$11\pi/3-\chi$	$3\pi-\chi$	$7\pi/3-\chi$

[a] ϕ and χ are mod 4π and $0 \leq \theta \leq \pi$.

From the results given in Eq. (18-27) we can draw up Table 18-6 for the effect of each element of $C_{3v}(M)^2$ on the Euler angles. Using these results the multiplication table for the group elements can be determined and this is given in Table 18-7. Since $R^2 = E$, and since R commutes with all the elements of an MS group, we only need to construct part of the multiplication table as done in Table 18-7. Using the multiplication table we can determine the class structure of the group (see Table 18-8) and determine the following class multiplication results:

$$\begin{aligned} C_4^2 &= C_1, \\ C_2C_4 &= C_5, \\ C_2C_5 &= C_2 + 2C_4, \\ C_3^2 &= 3C_4 + 3C_2, \\ C_3C_4 &= C_6. \end{aligned} \tag{18-28}$$

For the two-dimensional representations of $C_{3v}(M)^2$ we have $\chi[E] = \chi_1 = 2$ and the preceding equations lead to the following equations involving the characters (using Eq. (5-69))

$$\begin{aligned} \chi_4^2 &= 4, \\ \chi_2\chi_4 &= 2\chi_5, \\ \chi_2\chi_5 &= \chi_2 + \chi_4, \\ \chi_3^2 &= 2(\chi_4 + 2\chi_2)/3, \\ \chi_6 &= \chi_3\chi_4/2. \end{aligned} \tag{18-29}$$

From these equations we deduce the characters of the two-dimensional representations to be as given in Table 18-9. The characters of the irreducible representations can be deduced from the results in Table 18-9 and these are given in Table 18-10. In the character table of $C_{3v}(\mathrm{M})^2$ given in Table 18-20 the pair of separably degenerate irreducible representations are considered together as $E_{3/2}$ (see Tables 6-4 and 7-2, and the last two paragraphs of Section 7.4).

Table 18-7
Part of the multiplication table of the elements of the $C_{3v}(\mathrm{M})^2$ group[a]

		E	(123)	(132)	$(12)^*$	$(23)^*$	$(13)^*$
E	:	E	(123)	(132)	$(12)^*$	$(23)^*$	$(13)^*$
(123)	:	(123)	(132)	R	$R(13)^*$	$(12)^*$	$(23)^*$
(132)	:	(132)	R	$R(123)$	$R(23)^*$	$R(13)^*$	$(12)^*$
$(12)^*$	:	$(12)^*$	$(23)^*$	$(13)^*$	R	$R(123)$	$R(132)$
$(23)^*$	:	$(23)^*$	$(13)^*$	$R(12)^*$	(132)	R	$R(123)$
$(13)^*$	:	$(13)^*$	$R(12)^*$	$R(23)^*$	(123)	(132)	R

[a] Since $R^2 = E$, and since R commutes with all the elements of the group, the rest of the multiplication table can be easily derived from these results.

We could equally well have defined the Euler angle transformations of (132) and R(132) to be interchanged from the definition in Table 18-6, and $(23)^*$ and $R(23)^*$ to be similarly interchanged. If we did this the class structure would be as follows:

$$\begin{array}{llllll} E & (123) & (12)^* & R & R(123) & R(12)^* \\ & (132) & (23)^* & & R(132) & R(23)^* \\ & & (13)^* & & & R(13)^* \end{array} \tag{18-30}$$

By this renaming of some of the elements of $C_{3v}(\mathrm{M})^2$ we have achieved a neater looking class structure. This is pointed out to show that Euler angle transformations caused by O and RO (where O is any element of the MS group) can be interchanged and the choice is simply one of convenience in the spin double group.

Having set up the spin double groups of the MS groups, having determined the equivalent rotations for each of their operations, and having obtained the character tables of the groups, we can use the equivalent rotations of the MS groups to correlate the irreducible representations with the representations $D^{(j)}$ of $\boldsymbol{K}(\mathrm{mol})^2$ for j half-integral. These correlations are included in Appendix ***B***.

18.4 THE SPIN DOUBLE GROUPS OF NONRIGID MOLECULES

We consider the determination of the character table of the electron spin double group $\boldsymbol{G}_6{}^2$ of a molecule with an odd number of electrons that has the

Table 18-8

The class structure of the $C_{3v}(\mathrm{M})^2$ group

C_1	C_2	C_3	C_4	C_5	C_6
E	(123)	(12)*	R	R(123)	R(12)*
	R(132)	R(23)*		(132)	(23)*
		(13)*			R(13)*

Table 18-9

Characters of the two-dimensional representations of $C_{3v}(\mathrm{M})^2$ as obtained from the results in Eq. (18-29)

C_1	C_2	C_3	C_4	C_5	C_6
2	2	2	2	2	2
2	2	−2	2	2	−2
2	−1	0	2	−1	0
2	−2	$2i$	−2	2	$-2i$
2	−2	$-2i$	−2	2	$2i$
2	1	0	−2	−1	0

Table 18-10

Characters of the irreducible representations of $C_{3v}(\mathrm{M})^2$ as deduced from the results in Table 18-9

	C_1	C_2	C_3	C_4	C_5	C_6
A_1:	1	1	1	1	1	1
A_2:	1	1	−1	1	1	−1
E:	2	−1	0	2	−1	0
$E_{3/2}$:	1	−1	i	−1	1	$-i$
	1	−1	$-i$	−1	1	i
$E_{1/2}$:	2	1	0	−2	−1	0

geometrical structure of the CH_3OH molecule and for which the odd electron spin is coupled to the COH part of the molecule (e.g., perhaps CH_3SeH^+). We show that the character table is different if the odd electron spin is coupled to the CH_3 part of the molecule (e.g., perhaps, SiH_3OH^+).

Table 18-11

Transformation properties of Euler angles for $abc(\equiv zxy)$ principal axes of CH_3OH under the effect of elements of the $G_6{}^2$ group

E	$(12)^*$	R	$R(12)^*$
(123)	$(23)^*$	$R(123)$	$R(23)^*$
(132)	$(13)^*$	$R(132)$	$R(13)^*$
θ	$\pi-\theta$	θ	$\pi-\theta$
ϕ	$\phi+\pi$	ϕ	$\phi+\pi$
χ	$\pi-\chi$	$\chi+2\pi$	$3\pi-\chi$

The CH_3OH molecule and its principal axes of inertia are indicated in Table A-22. The COH plane is the ab plane. The orientation of the (a, b, c) axes in space is given by the Euler angles (θ, ϕ, χ) where we use a I^r convention ($abc \equiv zxy$). The effect of each of the elements of the group $G_6{}^2$ on the Euler angles [see Eqs. (18-8) and (18-9)] can be determined and is given in Table 18-11. Using the results in Table 18-11 we can determine the group multiplication table, and this is given in Table 18-12.

Table 18-12

Part[a] of the multiplication table of the elements of the group $G_6{}^2$

		E	(123)	(132)	$(12)^*$	$(23)^*$	$(13)^*$
E	:	E	(123)	(132)	$(12)^*$	$(23)^*$	$(13)^*$
(123)	:	(123)	(132)	E	$(13)^*$	$(12)^*$	$(23)^*$
(132)	:	(132)	E	(123)	$(23)^*$	$(13)^*$	$(12)^*$
$(12)^*$	:	$(12)^*$	$(23)^*$	$(13)^*$	R	$R(123)$	$R(132)$
$(23)^*$	:	$(23)^*$	$(13)^*$	$(12)^*$	$R(132)$	R	$R(123)$
$(13)^*$	:	$(13)^*$	$(12)^*$	$(23)^*$	$R(123)$	$R(132)$	R

[a] Since $R^2 = E$ and since R commutes with all the elements of the group G_6 the rest of the multiplication table can be easily constructed.

Using the multiplication table [see Eq. (5-49)] we can determine the class structure of $\boldsymbol{G}_6{}^2$ and this is given in Table 18-13. The class products can be determined [See Eq. (5-68)] and those that we use in constructing the character table are

$$\begin{aligned} C_2{}^2 &= 2C_1 + C_2, \\ C_4{}^2 &= C_1, \\ C_2C_4 &= C_5, \\ C_6{}^2 &= 3C_4 + 3C_5, \\ C_3C_4 &= C_6. \end{aligned} \tag{18-31}$$

Using Eqs. (5-69) and (18-31) we see that the characters of the two-dimensional representations of $\boldsymbol{G}_6{}^2$ satisfy

$$\begin{aligned} \chi_1 &= 2, \\ \chi_2{}^2 &= 2 + \chi_2, \\ \chi_4{}^2 &= 4, \\ \chi_2\chi_4 &= 2\chi_5, \\ 3\chi_6{}^2 &= 2(\chi_4 + 2\chi_5), \\ \chi_3\chi_4 &= 2\chi_6. \end{aligned} \tag{18-32}$$

Table 18-13

The class structures of the $\boldsymbol{G}_6{}^2$ group

C_1	C_2	C_3	C_4	C_5	C_6
E	(123) (132)	(12)* (23)* (13)*	R	R(123) R(132)	R(12)* R(23)* R(13)*

The characters for the two-dimensional representations of $\boldsymbol{G}_6{}^2$ that we obtain from these equations are given in Table 18-14. The characters of the irreducible representations follow directly from these results, and the character table is given in Table 18-24.

If the electron spin is coupled to the CH$_3$ group then we must introduce an axis system fixed to the CH$_3$ rotor. Doing this we obtain Euler angle transformations as given in Table 18-6, and thus we deduce that the character table of the spin double group is that of the $C_{3v}(\mathrm{M})^2$ group given in Table 18-20. The characters in the half-integral representations depend on which rotor fixed

Table 18-14

Characters of two-dimensional representations of group $G_6{}^2$ as determined from Eq. (18-32)

C_1	C_2	C_3	C_4	C_5	C_6
2	2	2	2	2	2
2	2	−2	2	2	−2
2	2	$2i$	−2	−2	$-2i$
2	2	$-2i$	−2	−2	$2i$
2	−1	0	2	−1	0
2	−1	0	−2	1	0

axis system the odd electron is coupled to by the spin–orbit coupling operator. The character table for the spin double group $G_{12}{}^2$ of the MS group of CH_3NO_2 obtained when the electron spin is 'tied' to the NO_2 rotor is given in Table 18-25. The character table for the situation when the spin is 'tied' to the CH_3 rotor is given in Table 18-26.

18.5 THE CLASSIFICATION OF ROTATIONAL WAVEFUNCTIONS HAVING HALF-INTEGRAL *J*

The determination of the species of the rotational wavefunctions of a molecule for half-integral values of the rotational quantum numbers has not been discussed above except by reduction of the species of the group $\boldsymbol{K}(\mathrm{mol})^2$, and we now do this by using the spin double group of the MS group.

The results in Eq. (12-46) and (12-47) for the transformation properties of the symmetric top functions $|J,k,m\rangle$ (with J integral) under the rotations $R_z{}^\beta$ and $R_\alpha{}^\pi$ were obtained from the transformation properties of $|J,0,0\rangle$ and the transformation properties of the ladder operators $\hat{J}_{\mathrm{m}}{}^{\pm}$ and $\hat{J}_{\mathrm{s}}{}^{\pm}$. For J half-integral we use the same technique except that we start with the function $|J,\frac{1}{2},\frac{1}{2}\rangle$ rather than the function $|J,0,0\rangle$. Using Eqs. (11-48) and (11-50) we obtain

$$|J,(\pm)|p|,\pm|m|\rangle = N_{\pm}^{(\pm)}(\hat{J}_{\mathrm{m}}{}^{(\mp)})^{|p|(\mp)(1/2)}(\hat{J}_{\mathrm{s}}{}^{\pm})^{|m|\mp(1/2)}|J,\frac{1}{2},\frac{1}{2}\rangle, \tag{18-33}$$

$$N_{\pm}^{(\pm)} = \left[\frac{(J-|p|)!(J-|m|)!}{(J+|p|)!(J+|m|)!}\right]^{1/2} \hbar^{-(|p|+|m|)} \left[\left(J+\frac{1}{2}\right)\hbar\right]^{\pm(1/2)(\pm)(1/2)}. \tag{18-34}$$

and J, p and m are half-integral. [Compare Eq. (11-52).]

From Eq. (11-15) we have (with an appropriate choice of phase factor)

$$\left|J,\frac{1}{2},\frac{1}{2}\right\rangle = \sqrt{\frac{2J+1}{8\pi^2}}\left(J+\frac{1}{2}\right)!\left(J-\frac{1}{2}\right)!e^{i(\phi+\chi)/2}\sum_{\sigma=0}^{J-(1/2)}(-1)^{J-(1/2)-\sigma}$$
$$\times\frac{(\cos\frac{1}{2}\theta)^{2\sigma+1}(\sin\frac{1}{2}\theta)^{2J-1-2\sigma}}{\sigma!(\sigma+1)![(J-\frac{1}{2}-\sigma)!]^2}. \qquad (18\text{-}35)$$

Reversing the order of the terms in the sum and writing $x = (J - \frac{1}{2} - \sigma)$ as the summation index we can rewrite this expression as

$$\left|J,\frac{1}{2},\frac{1}{2}\right\rangle = \sqrt{\frac{2J+1}{8\pi^2}}\left(J+\frac{1}{2}\right)!\left(J-\frac{1}{2}\right)!e^{i(\phi+\chi)/2}\sum_{x=0}^{J-(1/2)}(-1)^{x}$$
$$\times\frac{(\cos\frac{1}{2}\theta)^{2J-2x}(\sin\frac{1}{2}\theta)^{2x}}{(x!)^2(J+\frac{1}{2}-x)!(J-\frac{1}{2}-x)!}. \qquad (18\text{-}36)$$

Using Eq. (18-33) and the expression for $|J,\frac{1}{2},\frac{1}{2}\rangle$ in Eq. (18-36) we have

$$\left|J,-\frac{1}{2},\frac{1}{2}\right\rangle = \left[\hbar\left(J+\frac{1}{2}\right)\right]^{-1}\hat{J}_{\rm m}^{+}\left|J,\frac{1}{2},\frac{1}{2}\right\rangle \qquad (18\text{-}37)$$

$$= (-1)\sqrt{\frac{2J+1}{8\pi^2}}\left(J+\frac{1}{2}\right)!\left(J-\frac{1}{2}\right)!e^{i(\phi-\chi)/2}\sum_{\sigma=0}^{J-(1/2)}(-1)^{J-(1/2)-\sigma}$$
$$\times\frac{(\sin\frac{1}{2}\theta)^{2J-2\sigma}(\cos\frac{1}{2}\theta)^{2\sigma}}{(\sigma!)^2(J+\frac{1}{2}-\sigma)!(J-\frac{1}{2}-\sigma)!}$$
$$= (-1)^{J+(1/2)}\sqrt{\frac{2J+1}{8\pi^2}}\left(J+\frac{1}{2}\right)!\left(J-\frac{1}{2}\right)!e^{i(\phi-\chi)/2}\sum_{\sigma=0}^{J-(1/2)}(-1)^{\sigma}$$
$$\times\frac{(\sin\frac{1}{2}\theta)^{2J-2\sigma}(\cos\frac{1}{2}\theta)^{2\sigma}}{(\sigma!)^2(J+\frac{1}{2}-\sigma)!(J-\frac{1}{2}-\sigma)!}. \qquad (18\text{-}38)$$

Using Eqs. (18-36)–(18-38) we determine (see Table 12-1 for the definition of $R_z{}^{\beta}$ and $R_\alpha{}^{\pi}$) that

$$R_z{}^{\beta}\left|J,\frac{1}{2},\frac{1}{2}\right\rangle = e^{i\beta/2}\left|J,\frac{1}{2},\frac{1}{2}\right\rangle \qquad (18\text{-}39)$$

and

$$R_\alpha{}^{\pi}\left|J,\frac{1}{2},\frac{1}{2}\right\rangle = \exp\left[\frac{1}{2}i(3\pi-2\alpha)\right](-1)^{J+(1/2)}\left|J,-\frac{1}{2},\frac{1}{2}\right\rangle$$
$$= e^{i\pi J}e^{-i\alpha}\left[\hbar\left(J+\frac{1}{2}\right)\right]^{-1}\hat{J}_{\rm m}^{+}\left|J,\frac{1}{2},\frac{1}{2}\right\rangle. \qquad (18\text{-}40)$$

We can use Eqs. (18-39) and (18-40) in conjunction with Eqs. (12-36)–(12-39) for $\hat{J}_{\rm m}{}^{\pm}$ and $\hat{J}_{\rm s}{}^{\pm}$, and Eq. (18-33) for $|J,p,m\rangle$, to determine the transformation properties of the rotational function $|J,p,m\rangle$. The results obtained are

$$R_z{}^{\beta}|J,p,m\rangle = e^{ip\beta}|J,p,m\rangle \tag{18-41}$$

and

$$R_\alpha{}^{\pi}|J,p,m\rangle = e^{i\pi J}e^{-2i\alpha p}|J,-p,m\rangle, \tag{18-42}$$

where $J, p,$ and m are half-integral.

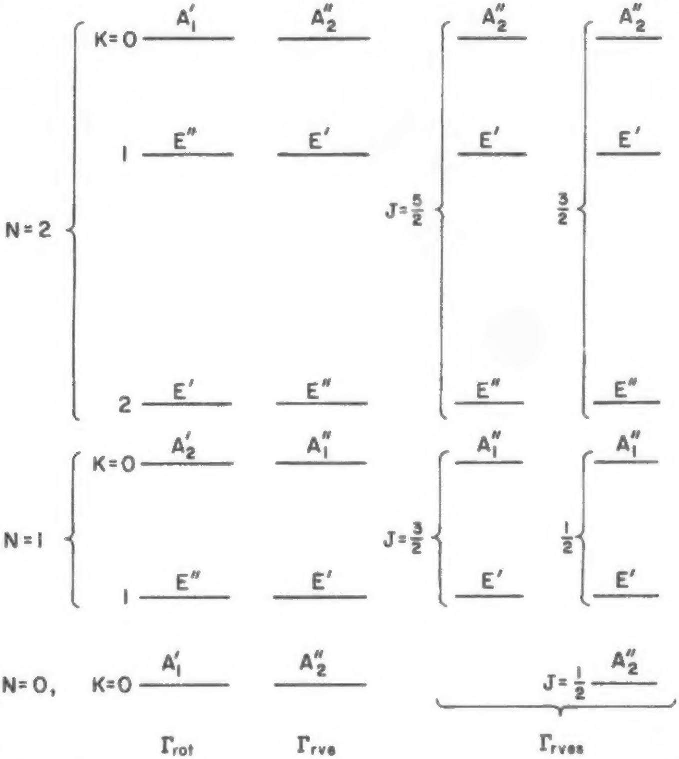

N=2
K=0
1
2
A′₁
E″
E′
A″₂
E′
E″
J=5/2
A″₂
E′
E″
3/2
A″₂
E′
E″
N=1
K=0
1
A′₂
E″
A″₁
E′
J=3/2
A″₁
E′
1/2
A″₁
E′
N=0,
K=0
A′₁
A″₂
J=1/2
A″₂
Γrot
Γrve
Γrves

Fig. 18-3. The symmetry labels $\Gamma_{\rm rves}$ for the rovibronic–electron spin energy levels of CH_3 in a $^2A_2''$ vibronic state using Hund's case (b) electron spin functions.

18.5.1 An example: CH_3

As an example of an application we consider the CH_3 radical which has a planar $^2A_2''$ electronic ground state; the spin double group of its MS group is the $\boldsymbol{D}_{3h}(\mathrm{M})^2$ group (see Table 18-23). Using space fixed electron spin functions [case (b)] the symmetry Γ_{rves} of the levels of a totally symmetric vibrational state of the $^2\mathrm{A}_2''$ electronic state can be determined using the results in Table 12-5 and these are given in Fig. 18-3. This figure is similar to Fig. 12-15 except that now we have $J = N \pm \frac{1}{2}$ and the extra symmetry distinctions ($'$) and ($''$) arising from the feasibility of E^*. Using molecule fixed spin functions [case (a)] we determine from the $\boldsymbol{K}(\mathrm{mol})^2 \rightarrow \boldsymbol{D}_{3h}(\mathrm{M})^2$ correlation table that the pair of $S = \frac{1}{2}$ spin functions generates the representation $E_{1/2}$ of $\boldsymbol{D}_{3h}(\mathrm{M})^2$. Multiplying this by the electron orbital species A_2'' we obtain $E_{5/2}$ as the electron spin–orbit species Γ_{eso}. The transformation properties of the rotational wavefunctions $|J, p, m\rangle$, with J half-integral, under the effect of the operations of the $\boldsymbol{D}_{3h}(\mathrm{M})^2$ group can be obtained from a knowledge of the equivalent rotations of the elements in conjunction with Eqs. (18-41) and (18-42). The characters of the representation generated by the pair of functions $|J, P, m\rangle$ and $|J, -P, m\rangle$ are [giving the characters in the order the elements are listed in Table 18-23 for $\boldsymbol{D}_{3h}(\mathrm{M})^2$]:

$$\begin{aligned} &2, 2\cos(2\pi P/3), 0, 2\cos(P\pi), 2\cos(-\pi P/3),\\ &\quad 0, 2\cos(2P\pi), 2\cos(8P\pi/3), 2\cos(5P\pi/3). \end{aligned} \tag{18-43}$$

This should be compared to Eq. (12-49). The symmetry species obtained are listed in Table 18-15.

Table 18-15

Symmetry species of case (a) rotational wavefunctions $|J, p, m\rangle$ of CH_3 in the $\boldsymbol{D}_{3h}(\mathrm{M})^2$ group[a]

P	Γ_{rot}	P	Γ_{rot}	P	Γ_{rot}
$6n \pm (\frac{1}{2})$	$E_{1/2}$	$6n \pm (\frac{3}{2})$	$E_{3/2}$	$6n \pm (\frac{5}{2})$	$E_{5/2}$

[a] n is integral; $P=|p|$ is positive half-integral.

In Fig. 18-4 the symmetry Γ_{rves} of the rovibronic–electron spin functions obtained using these results are given in a case (a) basis for CH_3 in the $^2A_2''$ state. The reader can correlate the levels of Figs. 18-3 and 18-4 if it is remembered that J and Γ_{rves} do not change. Note that Γ_{rves} is always single valued. For most polyatomic molecules the coupling of the electron spin to the molecular framework is small and a good understanding of the energy level pattern is obtained using a Hund's case (b) basis. In this case the energy level pattern is like that of a singlet state except for the fact that each level has a multiplicity of $2S + 1$ (or if $N < S$ the multiplicity is $2N + 1$).

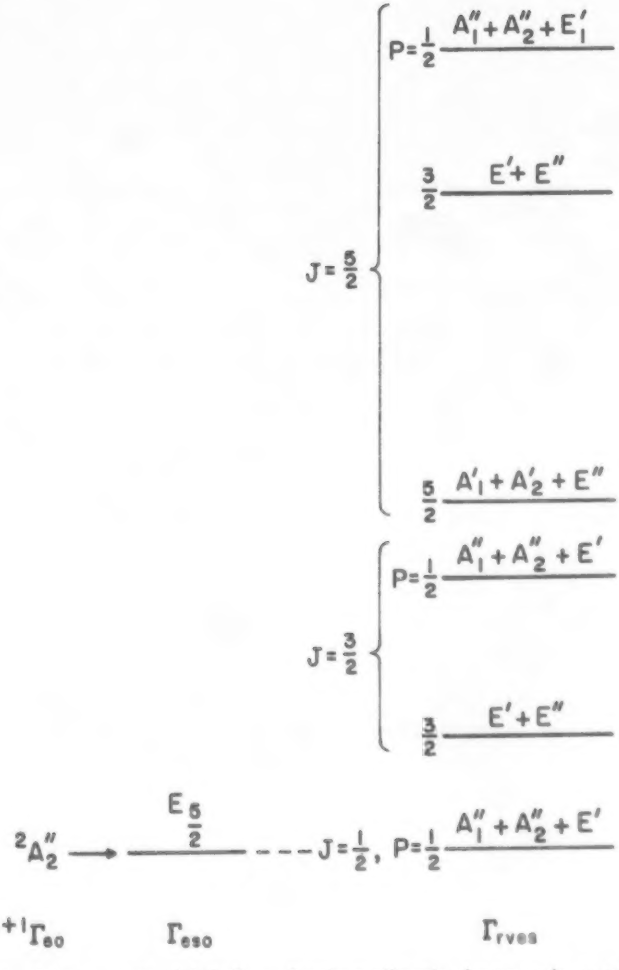

$J=\frac{5}{2}$
$P=\frac{1}{2}$ $A_1''+A_2''+E_1'$
$\frac{3}{2}$ $E'+E''$
$\frac{5}{2}$ $A_1'+A_2'+E''$
$J=\frac{3}{2}$
$P=\frac{1}{2}$ $A_1''+A_2''+E'$
$\frac{3}{2}$ $E'+E''$
$^2A_2''$
$E_{\frac{5}{2}}$
$J=\frac{1}{2}$, $P=\frac{1}{2}$ $A_1''+A_2''+E'$
$^{2S+1}\Gamma_{eo}$
Γ_{eso}
Γ_{rves}

Fig. 18-4. The symmetry labels Γ_{rves}, for the rovibronic–electron spin energy levels of CH_3 in a $^2A_2''$ electronic state (and an A_1 vibrational state) using Hund's case (a) electron spin functions.

APPENDIX 18-1: CHARACTER TABLES OF SOME SPIN DOUBLE GROUPS

Table 18-16

The group $C_s(M)^2$

$C_s(M)^2$:	E	E^*	R	
	1	2	1	
Equiv. rot.:	R^0	R_c^{π}	$R^{2\pi}$	
A':	1	1	1	
A'':	1	−1	1	
$E_{1/2}$:	2	0	−2	sep

Table 18-17

The group $C_i(M)^2$

$C_i(M)^2$:	E	$(12)(34)(56)(78)^*$	R	$R(12)(34)(56)(78)^*$
	1	1	1	1
Equiv. rot.:	R^0	R^0	$R^{2\pi}$	$R^{2\pi}$
A_g:	1	1	1	1
A_u:	1	−1	1	−1
$E_{g/2}$:	2	2	−2	−2
$E_{u/2}$:	2	−2	−2	2

The characters in $E_{g/2}$ and $E_{u/2}$ have been doubled since they come from type two corepresentations [Wigner (1959) page 343], also called case (b) [Dimmock and Wheeler (1964) page 733].

Table 18-18

The group $C_2(M)^2$

$C_2(M)^2$:	E	$(12)(34)$	R	
	1	2	1	
Equiv. rot.:	R^0	R_b^{π}	$R^{2\pi}$	
A:	1	1	1	
B:	1	−1	1	
$E_{1/2}$:	2	0	−2	sep

Table 18-19

The group $C_{2v}(M)^2$

$C_{2v}(M)^2$	E	(12)	E^*	$(12)^*$	R
	1	2	2	2	1
Equiv. rot.:	R^0	R_b^{π}	R_c^{π}	R_a^{π}	$R^{2\pi}$
A_1:	1	1	1	1	1
A_2:	1	1	−1	−1	1
B_1:	1	−1	−1	1	1
B_2:	1	−1	1	−1	1
$E_{1/2}$:	2	0	0	0	−2

Table 18-20

The group $C_{3v}(M)^2$

$C_{3v}(M)^2$:	E	(123)	$(23)^*$	R	$R(123)$	
	1	2	6	1	2	
Equiv. rot.:	R^0	$R_z^{2\pi/3}$	$R_{\pi/2}^{\pi}$	$R^{2\pi}$	$R_z^{8\pi/3}$	
A_1:	1	1	1	1	1	
A_2:	1	1	−1	1	1	
E:	2	−1	0	2	−1	
$E_{1/2}$:	2	1	0	−2	−1	
$E_{3/2}$:	2	−2	0	−2	2	: sep

Table 18-21

The group $D_{2h}(M)^2$

	E	(12)(34)	(13)(24)(56)	(14)(23)(56)	E^*	(12)(34)*	(13)(24)(56)*	(14)(23)(56)*	R	R(14)(23)(56)*
$D_{2h}(M)^2$:	1	2	2	2	2	2	2	1	1	1
Equiv. rot.:	R^0	R_a^π	R_b^π	R_c^π	R_c^π	R_b^π	R_a^π	R^0	$R^{2\pi}$	$R^{2\pi}$
A_g:	1	1	1	1	1	1	1	1	1	1
A_u:	1	1	1	1	−1	−1	−1	−1	1	−1
B_{1g}:	1	1	−1	−1	−1	−1	1	1	1	1
B_{1u}:	1	1	−1	−1	1	1	−1	−1	1	−1
B_{2g}:	1	−1	1	−1	−1	1	−1	1	1	1
B_{2u}:	1	−1	1	−1	1	−1	1	−1	1	−1
B_{3g}:	1	−1	−1	1	1	−1	−1	1	1	1
B_{3u}:	1	−1	−1	1	−1	1	1	−1	1	−1
$E_{g/2}$:	2	0	0	0	0	0	0	2	−2	−2
$E_{u/2}$:	2	0	0	0	0	0	0	−2	−2	2

Table 18-22

The group $C_{2h}(M)^2$

	E	(12)(34)(56)	E^*	(12)(34)(56)*	R	R(12)(34)(56)*		
$C_{2h}(M)^2$:	1	2	2	1	1	1		
Equiv. rot.:	R^0	R_c^π	R_c^π	R^0	$R^{2\pi}$	$R^{2\pi}$		
A_g:	1	1	1	1	1	1		
A_u:	1	1	−1	−1	1	−1		
B_g:	1	−1	−1	1	1	1		
B_u:	1	−1	1	−1	1	−1		
$E_{g/2}$:	2	0	0	2	−2	−2	:	sep
$E_{u/2}$:	2	0	0	−2	−2	2	:	sep

Table 18-23

The group $D_{3h}(M)^2$

$D_{3h}(M)^2$:	E 1	(123) 2	(23) 6	E^* 2	$(123)^*$ 2	$(23)^*$ 6	R 1	$R(123)$ 2	$R(123)^*$ 2
Equiv. rot.:	R^0	$R_z^{2\pi/3}$	R_0^{π}	R_z^{π}	$R_z^{-\pi/3}$	$R_{\pi/2}^{\pi}$	$R^{2\pi}$	$R_z^{8\pi/3}$	$R_z^{5\pi/3}$
A_1':	1	1	1	1	1	1	1	1	1
A_1'':	1	1	1	-1	-1	-1	1	1	-1
A_2':	1	1	-1	1	1	-1	1	1	1
A_2'':	1	1	-1	-1	-1	1	1	1	-1
E':	2	-1	0	2	-1	0	2	-1	-1
E'':	2	-1	0	-2	1	0	2	-1	1
$E_{1/2}$:	2	1	0	0	$\sqrt{3}$	0	-2	-1	$-\sqrt{3}$
$E_{3/2}$:	2	-2	0	0	0	0	-2	2	0
$E_{5/2}$:	2	1	0	0	$-\sqrt{3}$	0	-2	-1	$\sqrt{3}$

Table 18-24

The group $G_6{}^2$. Example: CH_3OH^+ when the axes are tied to the OH group

$G_6{}^2$:	E 1	(123) 2	$(23)^*$ 6	R 1	$R(123)$ 2	
Equiv. rot.:	R^0	R^0	$R_c{}^{\pi}$	$R^{2\pi}$	$R^{2\pi}$	
A_1:	1	1	1	1	1	
A_2:	1	1	-1	1	1	
E:	2	-1	0	2	-1	
$E_{5/2}$:	2	-1	0	-2	1	
$E_{1/2}$:	2	2	0	-2	-2	: sep

Table 18-25

The group $G_{12}{}^2$. Example: $CH_3NO_2^+$ when the axes are tied to the NO_2 group

G_{12}^2 :	E	(123)	(23)*	(45)	(123)(45)	(23)(45)*	R	R(123)	R(123)(45)
	1	2	6	2	2	6	1	2	2
Equiv. rot.:	R^0	R^0	$R_c{}^\pi$	$R_a{}^\pi$	$R_a{}^\pi$	$R_b{}^\pi$	$R^{2\pi}$	$R^{2\pi}$	$R_a^{3\pi}$
$A_1{}'$:	1	1	1	1	1	1	1	1	1
$A_1{}''$:	1	1	1	−1	−1	−1	1	1	−1
$A_2{}'$:	1	1	−1	1	1	−1	1	1	1
$A_2{}''$:	1	1	−1	−1	−1	1	1	1	−1
E' :	2	−1	0	2	−1	0	2	−1	−1
E'' :	2	−1	0	−2	1	0	2	−1	1
$E_{a/2}$:	2	−1	0	0	$\sqrt{3}$	0	−2	+1	$-\sqrt{3}$
$E_{1/2}$:	2	2	0	0	0	0	−2	−2	0
$E_{b/2}$:	2	−1	0	0	$-\sqrt{3}$	0	−2	+1	$\sqrt{3}$

Table 18-26

The character table of the spin double group for $CH_3NO_2^+$ obtained when the axes are tied to the CH_3 rotor

	E	(123)	(12)*	(45)	(123)(45)	(12)(45)*	R	R(123)	R(45)	R(123)(45)		
	1	2	6	1	2	6	1	2	1	2		
Equiv. rot.:	R^0	$R_z^{2\pi/3}$	$R^\pi_{\pi/6}$	R^0	$R_z^{2\pi/3}$	$R^\pi_{\pi/6}$	$R^{2\pi}$	$R_z^{8\pi/3}$	$R^{2\pi}$	$R_z^{8\pi/3}$		
$A_1{}'$:	1	1	1	1	1	1	1	1	1	1		
$A_1{}''$:	1	1	1	−1	−1	−1	1	1	−1	−1		
$A_2{}'$:	1	1	−1	1	1	−1	1	1	1	1		
$A_2{}''$:	1	1	−1	−1	−1	1	1	1	−1	−1		
E' :	2	−1	0	2	−1	0	2	−1	2	−1		
E'' :	2	−1	0	−2	1	0	2	−1	−2	1		
$E'_{1/2}$:	2	1	0	2	1	0	−2	−1	−2	−1		
$E''_{1/2}$:	2	−1	0	−2	1	0	−2	1	2	−1		
$E'_{3/2}$:	2	−2	0	2	−2	0	−2	2	−2	2	:	sep
$E''_{3/2}$:	2	−2	0	−2	2	0	−2	2	2	−2	:	sep

BIBLIOGRAPHICAL NOTES

Symmetry classification of electron spin functions

Altmann (1979), Altmann and Palacio (1979), and Altmann and Herzig (1982). We say that a group of matrices $\{D[P_1], D[P_2], D[P_3], \dots\}$ forms a representation of a group with elements $\{P_1, P_2, P_3, \dots\}$ when the following condition is fulfilled:

$$D[P_i]D[P_j] = D[P_{ij}] \text{ if } P_iP_j = P_{ij} \tag{18-44}$$

for arbitrary group elements P_i and P_j. The concept of a representation can be generalized to so-called *ray representations* (or *projective representations*) which fulfill the less restrictive equation:

$$D[P_i]D[P_j] = \epsilon(P_i, P_j)\, D[P_{ij}] \text{ if } P_iP_j = P_{ij}, \tag{18-45}$$

again for arbitrary group elements P_i and P_j [see Hamermesh (1964) and Hurley (1966)]. The quantity $\epsilon(P_i, P_j)$ is a phase factor [i.e., a complex number with $|\epsilon(P_i, P_j)|^2 = 1$] depending on P_i and P_j. Most of the time we generate representation matrices $D[P_i]$ that describe the effect of P_i on a quantum mechanical wavefunction as discussed in Chapter 6; see Eq. (6-51). From a quantum mechanical point of view the wavefunction $\epsilon(P_i, P_j)P_iP_j\Psi$ is equivalent to $P_iP_j\Psi$; the two wavefunctions describe the same physical situation. Hence it can be argued that the ray representation gives the same description of the group $\{P_1, P_2, P_3, \dots\}$ as the "true" representation defined by Eq. (18-44). Altmann (1979) has proposed a symmetry classification scheme for electron spin functions alternative to that described in the present chapter. He does not classify the functions in the electron spin double group but uses instead ray representations of the original group for the classification. Applications of the scheme are given by Altmann and Palacio (1979) and Altmann and Herzig (1982).

APPENDIX *A*

The Character Tables

This Appendix gives the character tables of the most common molecular symmetry (MS) groups and extended molecular symmetry (EMS) groups. The MS group is defined in Chapter 3. The EMS group is necessary for the classification of the vibronic states, and other basis states, of linear molecules and of nonrigid molecules (like dimethylacetylene) that have identical coaxial internal rotors. The EMS group is defined in Eqs. (17-99)–(17-112) for linear molecules, and in Sections 15.4.4–15.4.6 for nonrigid molecules that have identical coaxial internal rotors. The latter EMS groups contain the special symmetry operation E' which is the rotation of either of the two internal rotors through 2π radians, and which does nothing to the space fixed coordinates.

For a rigid nonlinear molecule the MS group is isomorphic to the molecular point group, and in such a case the name of the MS group is taken to be that of the point group followed by (M), e.g., the MS group of CH_3F is called $\boldsymbol{C}_{3v}$(M). For a linear rigid molecule the EMS group is isomorphic to the molecular point group and is called $\boldsymbol{C}_{\infty v}$(EM) or $\boldsymbol{D}_{\infty h}$(EM) as appropriate; the MS group of a linear molecule is called $\boldsymbol{C}_{\infty \mathrm{v}}(\mathrm{M})$ or $\boldsymbol{D}_{\infty \mathrm{h}}(\mathrm{M})$ but these are not isomorphic to the $\boldsymbol{C}_{\infty \mathrm{v}}$ or $\boldsymbol{D}_{\infty \mathrm{h}}$ point groups. For a nonrigid molecule the MS group is called $\boldsymbol{G}_n$, where n is the order of the group, and the EMS group for a molecule whose MS group is $\boldsymbol{G}_n$ is called $\boldsymbol{G}_n(\mathrm{EM})$. For rigid molecules the irreducible representations are named in the same way as for the (isomorphic) point group. The irreducible representations are ordered in each symmetry group according to established convention; the convention is necessary to ensure a consistent numbering system for the normal vibrations. The normal vibrations are numbered according to their symmetry species, and then within each symmetry species from highest to lowest wavenumber.

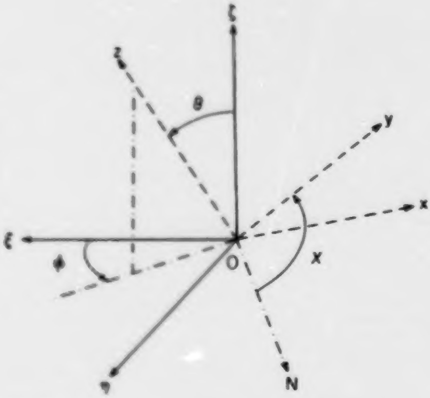


Fig. A-1. The definition of the Euler angles (θ, ϕ, χ) that relate the orientation of the molecule fixed (x, y, z) axes to the (ξ, η, ζ) axes. The origin of both axis systems is at the nuclear center of mass O, and the node line ON is directed so that a right handed screw is driven along ON in its positive direction by twisting it from ζ to z through θ where $0 \leq \theta \leq \pi$. ϕ and χ have the ranges 0 to 2π. χ is measured from the node line.

In each character table one element from each class is given and the number of elements in the class is indicated underneath the element. If the MS or EMS group is isomorphic to the molecular point group (this only happens for rigid molecules), the appropriate elements in each class of the molecular point group are given (this shows the effects of the MS or EMS group element on the vibronic variables), and the names of the irreducible representations are taken from the molecular point group. The equivalent rotation (Equiv. rot.) of the MS or EMS group element written for each class is also given. The equivalent rotations of an asymmetric top molecule are called R_a^{π}, R_b^{π}, or R_c^{π} to indicate rotations through π radians about the a, b, or c axis respectively. For a symmetric top molecule the equivalent rotations are called R_α^{π} or R_z^{β} as defined in Table A-1 which is a copy of Table 12-1. Knowing the equivalent rotations one can classify the components of the rovibronic angular momentum operator $\hat{J}_\alpha$ (see Table A-1). For further convenience we also give in Fig. A-1 a copy of Fig. 10-1 which defines the Euler angles.

The species obtained for the $\hat{J}_\alpha$ are indicated by placing the $\hat{J}_\alpha$ to the right of the appropriate irreducible representation. The rotational coordinate R_α [see Eq. (10-112)] transforms in the same way as $\hat{J}_\alpha$ under permutations and

Table A-1

The transformation properties[a] of the Euler angles and of the components of the rovibronic angular momentum $\hat{J}$

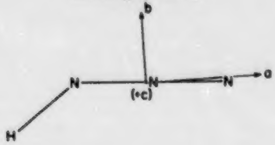
	R_α^π	R_z^β
θ	$\pi - \theta$	θ
ϕ	$\phi + \pi$	ϕ
χ	$2\pi - 2\alpha - \chi$	$\chi + \beta$
$\hat{J}_x$	$\hat{J}_x \cos 2\alpha + \hat{J}_y \sin 2\alpha$	$\hat{J}_x \cos\beta + \hat{J}_y \sin\beta$
$\hat{J}_y$	$\hat{J}_x \sin 2\alpha - \hat{J}_y \cos 2\alpha$	$-\hat{J}_x \sin\beta + \hat{J}_y \cos\beta$
$\hat{J}_z$	$-\hat{J}_z$	$\hat{J}_z$

[a] R_α^π is a rotation of the molecule fixed (x, y, z) axes through π radians about an axis in the xy plane making an angle α with the x axis (α is measured in the right handed sense about the z axis), and R_z^β is a rotation of the molecule fixed (x, y, z) axes through β radians about the z axis (β is measured in the right handed sense about the z axis). The expressions for the $\hat{J}_\alpha$ are given in Eqs. (10-84)-(10-86).

permutation-inversions. The translational coordinate T_α [see Eq. (10-111)] transforms in the same way as $\hat{J}_\alpha$ under a nuclear permutation but with opposite sign under a permutation-inversion (see Table 12-20), and the molecule fixed dipole moment components μ_α transform in the same way as the T_α [see Eq. (14-36)]. The species of the T_α, and of the components $\alpha_{\gamma\delta}$ of the electronic polarizability, given by the species of $T_\gamma T_\delta$ [see Eq. (14-138)], are also indicated by placing them the right of the appropriate irreducible representation. For molecules with a single internal rotation coordinate we have indicated, when possible, the symmetry of the torsional momentum operator $\hat{J}_\rho$. Finally the dipole representation Γ^* that has character +1 for the permutations and −1 for the permutation-inversions is indicated; allowed transitions are connected by this symmetry species as discussed in Chapter 14 [see Eq. (14-8)].

Table A-2

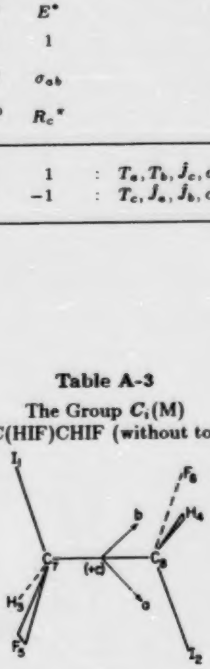
The group $C_s(M)$
Example: HN_3



$C_s(M)$:	E	E^*		
	1	1		
C_s:	E	σ_{ab}		
Equiv. rot.:	R^0	R_c^{π}		
A' :	1	1	:	$T_a, T_b, \hat{J}_c, \alpha_{aa}, \alpha_{bb}, \alpha_{cc}, \alpha_{ab}$
A'':	1	-1	:	$T_c, \hat{J}_a, \hat{J}_b, \alpha_{ac}, \alpha_{bc}, \Gamma^*$

Table A-3

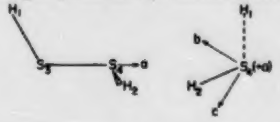
The Group $C_i(M)$
Example: Trans C(HIF)CHIF (without torsional tunneling)



$C_i(M)$:	E	$(12)(34)(56)(78)^*$		
	1	1		
C_i:	E	i		
Equiv. rot.:	R^0	R^0		
A_g:	1	1	:	$\hat{J}_a, \hat{J}_b, \hat{J}_c, \boldsymbol{\alpha}$
A_u:	1	-1	:	T_a, T_b, T_c, Γ^*

Table A-4

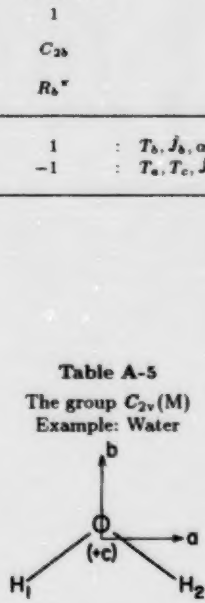
The group $C_2(M)$
Example: Hydrogen persulfide (without torsional tunneling)



$C_2(M)$:	E	$(12)(34)$		
	1	1		
C_2:	E	C_{2b}		
Equiv. rot.:	R^0	R_b^π		
A:	1	1	:	$T_b, \hat{J}_b, \alpha_{aa}, \alpha_{bb}, \alpha_{cc}, \alpha_{ac}, \Gamma^*$
B:	1	-1	:	$T_a, T_c, \hat{J}_a, \hat{J}_c, \alpha_{ab}, \alpha_{bc}$

Table A-5

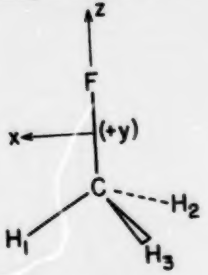
The group $C_{2v}(M)$
Example: Water



$C_{2v}(M)$:	E	(12)	E^*	$(12)^*$		
	1	1	1	1		
C_{2v}:	E	C_{2b}	σ_{ab}	σ_{bc}		
Equiv. rot.:	R^0	R_b^π	R_c^π	R_a^π		
A_1:	1	1	1	1	:	$T_b, \alpha_{aa}, \alpha_{bb}, \alpha_{cc}$
A_2:	1	1	-1	-1	:	$\hat{J}_b, \alpha_{ac}, \Gamma^*$
B_1:	1	-1	-1	1	:	$T_c, \hat{J}_a, \alpha_{bc}$
B_2:	1	-1	1	-1	:	$T_a, \hat{J}_c, \alpha_{ab}$

Table A-6

The group $C_{3v}(\mathrm{M})$
Example: Methyl fluoride



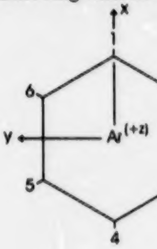
	E	(123)	$(23)^*$	
$C_{3v}(\mathrm{M})$:	1	2	3	
C_{3v}:	E	$2C_3$	$3\sigma_v$	
Equiv. rot.:	R^0	$R_z^{2\pi/3}$	$R_{\pi/2}^{\pi}$	
A_1:	1	1	1	: $T_z, \alpha_{zz}, \alpha_{xx} + \alpha_{yy}$
A_2:	1	1	−1	: $\hat{J}_z, \Gamma^*$
E:	2	−1	0	: $(T_x, T_y), (\hat{J}_x, \hat{J}_y), (\alpha_{xz}, \alpha_{yz}), (\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$

Table A-7

The group $C_{6v}(M)$

Example: Benzene-argon dimer[a]

(The argon atom is above the benzene ring with no tunneling to the other side of the ring).



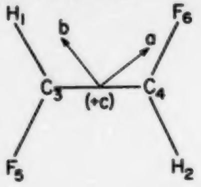
$C_{6v}(M)$:	E	(123456)	$(135)(246)$	$(14)(25)(36)$	$(26)(35)^*$	$(14)(23)(56)^*$	
	1	2	2	1	3	3	
C_{6v}:	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$	
Equiv. rot.:	R^0	$R_z^{\pi/3}$	$R_z^{2\pi/3}$	R_z^{π}	$R_{\pi/2}^{\pi}$	R_0^{π}	
A_1:	1	1	1	1	1	1	: $T_z, \alpha_{zz}, \alpha_{xx} + \alpha_{yy}$
A_2:	1	1	1	1	−1	−1	: $\hat{J}_z, \Gamma^*$
B_1:	1	−1	1	−1	1	−1	
B_2:	1	−1	1	−1	−1	1	
E_1:	2	1	−1	−2	0	0	: $(T_x, T_y), (\hat{J}_x, \hat{J}_y), (\alpha_{xz}, \alpha_{yz})$
E_2:	2	−1	−1	2	0	0	: $(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$

---

[a] See van der Avoird (1993). The pairs of bonded CH nuclei of the benzene moiety are labeled 1 through 6.

Table A-8

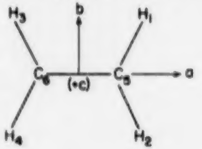
The group $C_{2h}(M)$
Example: Trans-difluoroethylene (without torsional tunneling)



$C_{2h}(M)$:	E	(12)(34)(56)	E^*	$(12)(34)(56)^*$	
	1	1	1	1	
C_{2h}:	E	C_{2c}	σ_{ab}	i	
Equiv. rot.:	R^0	R_c^{π}	R_c^{π}	R^0	
A_g:	1	1	1	1	: $\hat{J}_c, \alpha_{aa}, \alpha_{bb}, \alpha_{cc}, \alpha_{ab}$
A_u:	1	1	−1	−1	: T_c, Γ^*
B_g:	1	−1	−1	1	: $\hat{J}_a, \hat{J}_b, \alpha_{ac}, \alpha_{bc}$
B_u:	1	−1	1	−1	: T_a, T_b

Table A-9

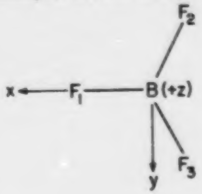
The group $D_{2h}(\mathrm{M})$
Example: Ethylene (without torsional tunneling)



$D_{2h}(\mathrm{M})$:	E	(12)(34)	(13)(24)(56)	(14)(23)(56)	E^*	(12)(34)*	(13)(24)(56)*	(14)(23)(56)*	
	1	1	1	1	1	1	1	1	
D_{2h}:	E	C_{2a}	C_{2b}	C_{2c}	σ_{ab}	σ_{ac}	σ_{bc}	i	
Equiv. rot.:	R^0	R_a^π	R_b^π	R_c^π	R_c^π	R_b^π	R_a^π	R^0	
A_g:	1	1	1	1	1	1	1	1	: $\alpha_{aa}, \alpha_{bb}, \alpha_{cc}$
A_u:	1	1	1	1	−1	−1	−1	−1	: Γ^*
B_{1g}:	1	1	−1	−1	−1	−1	1	1	: $\hat{J}_a, \alpha_{bc}$
B_{1u}:	1	1	−1	−1	1	1	−1	−1	: T_a
B_{2g}:	1	−1	1	−1	−1	1	−1	1	: $\hat{J}_b, \alpha_{ac}$
B_{2u}:	1	−1	1	−1	1	−1	1	−1	: T_b
B_{3g}:	1	−1	−1	1	1	−1	−1	1	: $\hat{J}_c, \alpha_{ab}$
B_{3u}:	1	−1	−1	1	−1	1	1	−1	: T_c

Table A-10

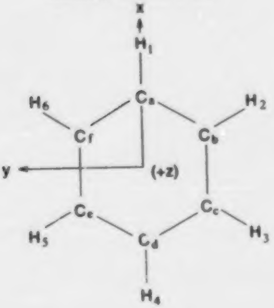
The group D_{3h}(M)
Example: Boron trifluoride



D_{3h}(M):	E	(123)	(23)	E^*	$(123)^*$	$(23)^*$		
	1	2	3	1	2	3		
D_{3h}:	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
Equiv. rot.:	R^0	$R_z^{2\pi/3}$	R_0^π	R_z^π	$R_z^{-\pi/3}$	$R_{\pi/2}^\pi$		
$A_1{}'$:	1	1	1	1	1	1	:	$\alpha_{zz}, \alpha_{xx} + \alpha_{yy}$
$A_1{}''$:	1	1	1	−1	−1	−1	:	Γ^*
$A_2{}'$:	1	1	−1	1	1	−1	:	$\hat{J}_z$
$A_2{}''$:	1	1	−1	−1	−1	1	:	T_z
E' :	2	−1	0	2	−1	0	:	$(T_x, T_y), (\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
E'':	2	−1	0	−2	1	0	:	$(\hat{J}_x, \hat{J}_y), (\alpha_{xz}, \alpha_{yz})$

Table A-11

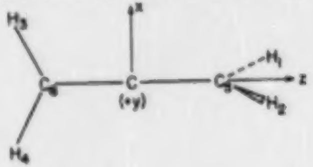
The group $D_{6h}(M)$
Example: Benzene



$D_{6h}(M)$:	E	(123456)(abcdef)	(135)(246)(ace)(bdf)	(14)(25)(36)(ad)(be)(cf)	(26)(35)(bf)(ce)	(14)(23)(56)(ad)(bc)(ef)	(14)(25)(36)(ad)(be)(cf)*	(135)(246)(ace)(bdf)*	(123456)(abcdef)*	E^*	(14)(23)(56)(ad)(bc)(ef)*	(26)(35)(bf)(ce)*		
	1	2	2	1	3	3	1	2	2	1	3	3		
D_{6h}:	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
Equiv. rot.:	R^0	$R_z^{\pi/3}$	$R_z^{2\pi/3}$	R_z^{π}	R_0^{π}	$R_{\pi/2}^{\pi}$	R^0	$R_z^{5\pi/3}$	$R_z^{4\pi/3}$	R_z^{π}	R_0^{π}	$R_{\pi/2}^{\pi}$		
A_{1g}:	1	1	1	1	1	1	1	1	1	1	1	1	:	α_{zz}, $\alpha_{xx} + \alpha_{yy}$
A_{1u}:	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	:	Γ^*
A_{2g}:	1	1	1	1	−1	−1	1	1	1	1	−1	−1	:	$\hat{J}_z$
A_{2u}:	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	:	T_z
B_{1g}:	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
B_{1u}:	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
B_{2g}:	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1		
B_{2u}:	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1		
E_{1g}:	2	1	−1	−2	0	0	2	1	−1	−2	0	0	:	$(\hat{J}_x, \hat{J}_y)$, $(\alpha_{xz}, \alpha_{yz})$
E_{1u}:	2	1	−1	−2	0	0	−2	−1	1	2	0	0	:	(T_x, T_y)
E_{2g}:	2	−1	−1	2	0	0	2	−1	−1	2	0	0	:	$(\alpha_{xy}$, $\alpha_{xx} - \alpha_{yy})$
E_{2u}:	2	−1	−1	2	0	0	−2	1	1	−2	0	0		

Table A-12

The group D_{2d}(M)
Example: Allene (without torsional tunneling)

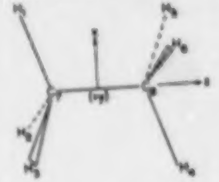


	E	$(1423)(56)^*$	$(12)(34)$	$(13)(24)(56)$	$(34)^*$	
D_{2d}(M):	1	2	1	2	2	
D_{2d}:	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$	
Equiv. rot.:	R^0	$R_z^{3\pi/2}$	R_z^π	$R_{3\pi/4}^\pi$	R_0^π	
A_1:	1	1	1	1	1	: $\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$
A_2:	1	1	1	−1	−1	: J_z
B_1:	1	−1	1	1	−1	: $\alpha_{xx}-\alpha_{yy}, \Gamma^*$
B_2:	1	−1	1	−1	1	: T_z, α_{xy}
E:	2	0	−2	0	0	: $(T_x, T_y), (J_x, J_y), (\alpha_{xz}, \alpha_{yz})$

Table A-13

The group D_{3d}(M)

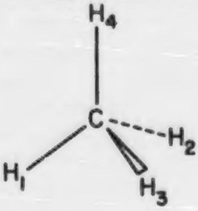
Example: Ethane (without torsional tunneling in the staggered conformation)



	E	$(123)(465)$	$(16)(24)(35)(78)$	$(14)(26)(35)(78)^*$	$(163425)(78)^*$	$(12)(46)^*$	
D_{3d}(M):	1	2	3	1	2	3	
D_{3d}:	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$	
Equiv. rot.:	R^0	$R_z^{2\pi/3}$	$R^{\pi}_{\pi/6}$	R^0	$R_z^{2\pi/3}$	$R^{\pi}_{\pi/6}$	
A_{1g}:	1	1	1	1	1	1	: $\alpha_{zz}, \alpha_{xx}+\alpha_{yy}$
A_{1u}:	1	1	1	−1	−1	−1	: Γ^*
A_{2g}:	1	1	−1	1	1	−1	: $\hat{J}_z$
A_{2u}:	1	1	−1	−1	−1	1	: T_z
E_g:	2	−1	0	2	−1	0	: $\left\{\begin{array}{l}(\hat{J}_x, \hat{J}_y), (\alpha_{xz}, \alpha_{yz}) \\ (\alpha_{xx}-\alpha_{yy}, \alpha_{xy})\end{array}\right.$
E_u:	2	−1	0	−2	1	0	: (T_x, T_y)

Table A-14

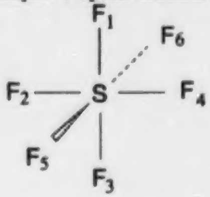
The group $T_d(M)$
Example: Methane



$T_d(M)$:	E	(123)	$(14)(23)$	$(1423)^*$	$(23)^*$		
	1	8	3	6	6		
T_d:	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1:	1	1	1	1	1	:	$\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$
A_2:	1	1	1	−1	−1	:	Γ^*
E:	2	−1	2	0	0	:	$(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy})$
F_1:	3	0	−1	1	−1	:	(J_x, J_y, J_z)
F_2:	3	0	−1	−1	1	:	$(T_x, T_y, T_z), (\alpha_{xy}, \alpha_{yz}, \alpha_{xz})$

Table A-15

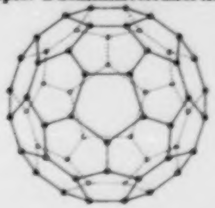
The group $O_h(M)$
Example: Sulphur hexafluoride



$O_h(M)$:	E	(145)(263)	(13)(26)(45)	(1234)	(13)(24)	(13)(24)(56)*	(125346)*	(25)(46)*	(1432)(56)*	(56)*		
	1	8	6	6	3	1	8	6	6	3		
O_h:	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$8S_6$	$6\sigma_d$	$6S_4$	$3\sigma_h$		
A_{1g}:	1	1	1	1	1	1	1	1	1	1	:	$\alpha_{zz}+\alpha_{xx}+\alpha_{yy}$
A_{1u}:	1	1	1	1	1	−1	−1	−1	−1	−1	:	Γ^*
A_{2g}:	1	1	−1	−1	1	1	1	−1	−1	1		
A_{2u}:	1	1	−1	−1	1	−1	−1	1	1	−1		
E_g:	2	−1	0	0	2	2	−1	0	0	2	:	$(2\alpha_{zz}-\alpha_{xx}-\alpha_{yy},$ $\alpha_{xx}-\alpha_{yy})$
E_u:	2	−1	0	0	2	−2	1	0	0	−2		
F_{1g}:	3	0	−1	1	−1	3	0	−1	1	−1	:	$(\hat{J}_x, \hat{J}_y, \hat{J}_z)$
F_{1u}:	3	0	−1	1	−1	−3	0	1	−1	1	:	(T_x, T_y, T_z)
F_{2g}:	3	0	1	−1	−1	3	0	1	−1	−1	:	$(\alpha_{xz}, \alpha_{yz}, \alpha_{x}$ [illegible]
F_{2u}:	3	0	1	−1	−1	−3	0	−1	1	1		

Table A-16

The group $I_h(\mathrm{M})$
Example: Buckminsterfullerene C_{60}



$I_h(\mathrm{M})$:	E	C_2	C_3	C_4	C_5	$\hat{O}_i$	C_7	C_8	C_9	C_{10}		
	1	12	12	20	15	1	12	12	20	15		
I_h:	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}^3$	$12S_{10}$	$20S_6$	15σ		
A_g:	1	1	1	1	1	1	1	1	1	1	:	$\alpha_{zz}+\alpha_{xx}+\alpha_{yy}$
A_u:	1	1	1	1	1	-1	-1	-1	-1	-1	:	Γ^*
F_{1g}:	3	η^+	η^-	0	-1	3	η^+	η^-	0	-1	:	(J_x, J_y, J_z)
F_{1u}:	3	η^+	η^-	0	-1	-3	$-\eta^+$	$-\eta^-$	0	1	:	(T_x, T_y, T_z)
F_{2g}:	3	η^-	η^+	0	-1	3	η^-	η^+	0	-1		
F_{2u}:	3	η^-	η^+	0	-1	-3	$-\eta^-$	$-\eta^+$	0	1		
G_g:	4	-1	-1	1	0	4	-1	-1	1	0		
G_u:	4	-1	-1	1	0	-4	1	1	-1	0		
H_g:	5	0	0	-1	1	5	0	0	-1	1	:	$(2\alpha_{zz}-\alpha_{xx}-\alpha_{yy},$ $\alpha_{xx}-\alpha_{yy},$ $\alpha_{xz}, \alpha_{yz}, \alpha_{xy})$
H_u:	5	0	0	-1	1	-5	0	0	1	-1		

$\eta^{\pm} = (1 \pm \sqrt{5})/2$. Each of the MS group operations involves the 60 indices labeling the nuclei in C_{60} [see Fig. 8-2] and we do not show the operations here. The elements in each class are described as follows:

C_2 Each operation is a product of 12 five-cycles $(abcde)$.

C_3 Each operation is a product of 12 five-cycles $(abcde)$.

C_4 Each operation is a product of 20 three-cycles (abc).

C_5 Each operation is a product of 30 transpositions (ab).

$\hat{O}_i$ The product of 30 transpositions (ab) and the inversion E^* [see Eq. (8-37)].

C_7 $= C_2\hat{O}_i$. Each operation is the product of six ten-cycles $(abcdefghij)$ and the inversion E^*.

C_8 $= C_3\hat{O}_i$. Each operation is the product of six ten-cycles $(abcdefghij)$ and the inversion E^*.

C_9 $= C_4\hat{O}_i$. Each operation is the product of 10 six-cycles $(abcdef)$ and the inversion E^*.

C_{10} $= C_5\hat{O}_i$. Each operation is the product of 30 transpositions (ab) and the inversion E^*.

$C_k = C_j\hat{O}_i$ indicates that the elements in C_k are obtained by combining each element in C_j with $\hat{O}_i$ [see Section 8.4.3]. From Fig. 8-2 the reader can construct the expressions for the MS group operations of C_{60}.

Table A-17

The group $C_{\infty v}(M)$
Example: Hydrogen cyanide
H——C——N

$C_{\infty v}(M)$:	E	E^*	
$\Sigma^+, +$:	1	1	
$\Sigma^-, -$:	1	−1	: Γ^*

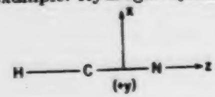
Table A-18

The group $D_{\infty h}(M)$
Example: Carbon dioxide
O_1——C——O_2

$D_{\infty h}(M)$:	E	(12)	E^*	$(12)^*$	
$\Sigma_g^+, +s$:	1	1	1	1	
$\Sigma_u^+, +a$:	1	−1	1	−1	
$\Sigma_g^-, -a$:	1	−1	−1	1	
$\Sigma_u^-, -s$:	1	1	−1	−1	: Γ^*

Table A-19

The group[a] $C_{\infty v}(EM)$
Example: Hydrogen cyanide

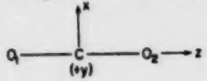


$C_{\infty v}(EM)$	E_0	E_ε	$\cdots$	∞E_ε^*	
	1	2	$\cdots$	∞	
$C_{\infty v}$:	E	$2C_\infty^\varepsilon$	$\cdots$	$\infty\sigma_v^{(\varepsilon/2)}$	
Equiv. rot.:	R^0	$R_z^{-\varepsilon}$	$\cdots$	$R^\pi_{(\pi+\varepsilon)/2}$	
$(+)\Sigma^+$:	1	1	$\cdots$	1	: $T_z, \alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
$(-)\Sigma^-$:	1	1	$\cdots$	−1	: $\hat{J}_z, \Gamma^*$
Π:	2	$2\cos\varepsilon$	$\cdots$	0	: $(T_x, T_y), (\hat{J}_x, \hat{J}_y), (\alpha_{xz}, \alpha_{yz})$
Δ:	2	$2\cos 2\varepsilon$	$\cdots$	0	: $(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
$\vdots$	$\vdots$	$\vdots$	$\cdots$	$\vdots$	

[a] The xyz axes are the $x'y'z'$ axes introduced in Chapter 17 for the isomorphic Hamiltonian.

Table A-20

The group[a] $D_{\infty h}$(EM)
Example: Carbon dioxide

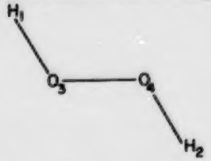


$D_{\infty h}$(EM):	E_0	E_ε	$\cdots$	∞E_ε^*	$(12)_\pi^*$	$(12)^*_{\pi+\varepsilon}$	$\cdots$	$\infty(12)_\varepsilon$		
	1	2	$\cdots$	∞	1	2	$\cdots$	∞		
$D_{\infty h}$:	E	$2C_\infty^\varepsilon$	$\cdots$	$\infty\sigma_v^{(\varepsilon/2)}$	i	$2S_\infty^{\pi+\varepsilon}$	$\cdots$	$\infty C_2^{(\varepsilon/2)}$		
Equiv. rot.:	R^0	$R_z^{-\varepsilon}$	$\cdots$	$R^\pi_{(\pi+\varepsilon)/2}$	R^0	$R_z^{-\varepsilon}$	$\cdots$	$R^\pi_{\varepsilon/2}$		
$(+s)\Sigma_g^+$:	1	1	$\cdots$	1	1	1	$\cdots$	1	:	$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$
$(+a)\Sigma_u^+$:	1	1	$\cdots$	1	-1	-1	$\cdots$	-1	:	T_z
$(-a)\Sigma_g^-$:	1	1	$\cdots$	-1	1	1	$\cdots$	-1	:	J_z
$(-s)\Sigma_u^-$:	1	1	$\cdots$	-1	-1	-1	$\cdots$	1	:	Γ^*
Π_g:	2	$2\cos\varepsilon$	$\cdots$	0	2	$2\cos\varepsilon$	$\cdots$	0	:	$(J_x, J_y), (\alpha_{xz}, \alpha_{yz})$
Π_u:	2	$2\cos\varepsilon$	$\cdots$	0	-2	$-2\cos\varepsilon$	$\cdots$	0	:	(T_x, T_y)
Δ_g:	2	$2\cos 2\varepsilon$	$\cdots$	0	2	$2\cos 2\varepsilon$	$\cdots$	0	:	$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$
Δ_u:	2	$2\cos 2\varepsilon$	$\cdots$	0	-2	$-2\cos 2\varepsilon$	$\cdots$	0	:	
⋮	⋮	⋮	$\cdots$	⋮	⋮	⋮	$\cdots$	⋮		

[a] The xyz axes are the $x'y'z'$ axes introduced in Chapter 17 for the isomorphic Hamiltonian.

Table A-21

The group G_4
Example: Hydrogen peroxide
(with torsional tunneling)



		G_4 :	E	$(12)(34)$	E^*	$(12)(34)^*$	
Γ_1[a]	Γ_2[b]	Γ_3[c] :	1	1	1	1	
A^+	A_g	A_1 :	1	1	1	1	
A^-	A_u	A_2 :	1	1	-1	-1	: Γ^*
B^-	B_g	B_1 :	1	-1	-1	1	
B^+	B_u	B_2 :	1	-1	1	-1	

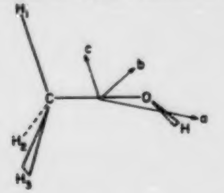
[a] Γ_1 notation based on effects of $(12)(34)$ and E^*.

[b] Γ_2 notation based on C_{2h} notation.

[c] Γ_3 notation based on C_{2v} notation.

Table A-22

The group G_6
Example: Methanol (with torsional tunneling)

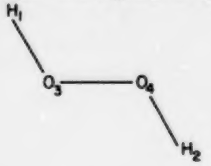


G_6:	E	(123)	$(23)^*$		
	1	2	3		
Equiv. rot.:	R^0	R^0	R_c^{π}		
A_1 :	1	1	1	:	$T_a, T_b, \hat{J}_c, \alpha_{aa}, \alpha_{bb}, \alpha_{cc}, \alpha_{ab}$
A_2 :	1	1	-1	:	$T_c, \hat{J}_a, \hat{J}_b, \hat{J}_\rho, \alpha_{ac}, \alpha_{bc}, \Gamma^*$
E :	2	-1	0		

Table A-23

The group G_8

Example: CNPI group of H_2O_2

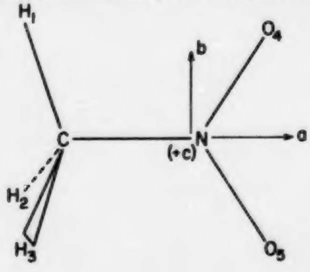


G_8 :	E	(12)(34)	E^*	(12)(34)*	(12)	(34)	(12)*	(34)*	
A_1' :	1	1	1	1	1	1	1	1	
A_1'' :	1	1	1	1	−1	−1	−1	−1	
A_2' :	1	1	−1	−1	1	1	−1	−1	: Γ^*
A_2'' :	1	1	−1	−1	−1	−1	1	1	
B_1' :	1	−1	−1	1	1	−1	−1	1	
B_1'' :	1	−1	−1	1	−1	1	1	−1	
B_2' :	1	−1	1	−1	1	−1	1	−1	
B_2'' :	1	−1	1	−1	−1	1	−1	1	

Table A-24

The group G_{12}

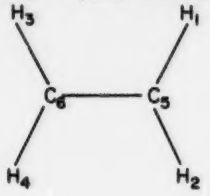
Example: Nitromethane (with torsional tunneling)



G_{12} :	E 1	(123) 2	(23)* 3	(45) 1	(123)(45) 2	(23)(45)* 3	
Equiv. rot.:	R^0	R^0	R_c^π	R_a^π	R_a^π	R_b^π	
A_1' :	1	1	1	1	1	1	: $T_a, \alpha_{aa}, \alpha_{bb}, \alpha_{cc}$
A_1'' :	1	1	1	−1	−1	−1	: $T_b, \hat{J}_c, \alpha_{ab}$
A_2' :	1	1	−1	1	1	−1	: $\hat{J}_a, \hat{J}_\rho, \alpha_{bc}, \Gamma^*$
A_2'' :	1	1	−1	−1	−1	1	: $T_c, \hat{J}_b, \alpha_{ac}$
E' :	2	−1	0	2	−1	0	
E'' :	2	−1	0	−2	1	0	

Table A-25

The group G_{16}
Example: Ethylene (with torsional tunneling)



G_{16} :		E	(1423)(56)*	(12)(34)	(13)(24)(56)	(34)*	E^*	(1423)(56)	(12)(34)*	(13)(24)(56)*	(34)	
		1	2	1	2	2	1	2	1	2	2	
MW[a]	LH[b]											
A_1^+	A_1^+ :	1	1	1	1	1	1	1	1	1	1	
A_2^+	A_2^+ :	1	1	1	−1	−1	1	1	1	−1	−1	
B_1^+	B_2^+ :	1	−1	1	1	−1	1	−1	1	1	−1	
B_2^+	B_1^+ :	1	−1	1	−1	1	1	−1	1	−1	1	
E^+	E^+ :	2	0	−2	0	0	2	0	−2	0	0	
A_1^-	B_2^- :	1	1	1	1	1	−1	−1	−1	−1	−1	
A_2^-	B_1^- :	1	1	1	−1	−1	−1	−1	−1	1	1	
B_1^-	A_1^- :	1	−1	1	1	−1	−1	1	−1	−1	1	: Γ^*
B_2^-	A_2^- :	1	−1	1	−1	1	−1	1	−1	1	−1	
E^-	E^- :	2	0	−2	0	0	−2	0	2	0	0	

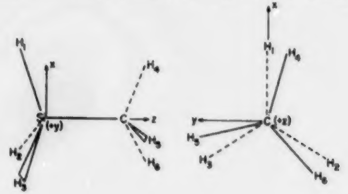
[a] Notation from Merer and Watson (1973). This correlates appropriately to D_{2d}(M) (see Table A-12).

[b] Notation from Longuet-Higgins (1963).

Table A-26

The group G_{18}

Example: Methylsilane (with torsional tunneling)


H1
x
Si (+y)
C
z
H4
H2
H3
H5
H6
x
H1
H4
y
C (+z)
H5
H3
H2
H6

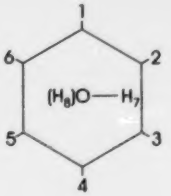
G_{18} :	E	(456)	(123)	(123)(456)	(123)(465)	(23)(56)*		
	1	2	2	2	2	9		
Equiv. rot.:	R^0	R^0	$R_z^{2\pi/3}$	$R_z^{2\pi/3}$	$R_z^{2\pi/3}$	$R_{\pi/2}^{\pi}$		
A_1 :	1	1	1	1	1	1	:	$T_z, \alpha_{zz}, \alpha_{xx} + \alpha_{yy}$
A_2 :	1	1	1	1	1	-1	:	$\hat{J}_z, \hat{J}_\rho, \Gamma^*$
E_1 :	2	2	-1	-1	-1	0	:	$(T_x, T_y), (\hat{J}_x, \hat{J}_y), (\alpha_{xz}, \alpha_{yz}), (\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
E_2 :	2	-1	2	-1	-1	0		
E_3 :	2	-1	-1	2	-1	0		
E_4 :	2	-1	-1	-1	2	0		

Table A-27

The group G_{24}

Example: Benzene-water dimer[a]

(The water moiety is above the benzene ring and we assume that (123456) and (78) are feasible; see page 49).



G_{24}:	E	(123456)	(135)(246)	(14)(25)(36)	(26)(35)*	(14)(23)(56)*	(78)	(123456)(78)	(135)(246)(78)	(14)(25)(36)(78)	(26)(35)(78)*	(14)(23)(56)(78)*	
	1	2	2	1	3	3	1	2	2	1	3	3	
A_{1s}:	1	1	1	1	1	1	1	1	1	1	1	1	
A_{2s}:	1	1	1	1	−1	−1	1	1	1	1	−1	−1	: Γ^*
B_{1s}:	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	
B_{2s}:	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1	
E_{1s}:	2	1	−1	−2	0	0	2	1	−1	−2	0	0	
E_{2s}:	2	−1	−1	2	0	0	2	−1	−1	2	0	0	
A_{1a}:	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	
A_{2a}:	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	
B_{1a}:	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1	
B_{2a}:	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1	
E_{1a}:	2	1	−1	−2	0	0	−2	−1	1	2	0	0	
E_{2a}:	2	−1	−1	2	0	0	−2	1	1	−2	0	0	

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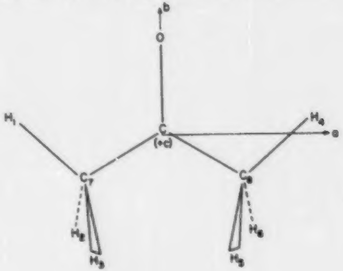
[a] See Table 9 of Gregory and Clary (1996), but we use s/a instead of +/−, and we exchange B_1 and B_2 labels (see Table A-7). Pairs of bonded CH nuclei are labeled 1 through 6.

Table A-28

The group G_{36}

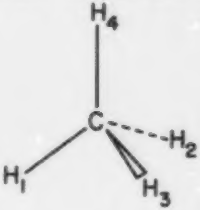
Example: Acetone (with torsional tunneling)



G_{36}:	E 1	(123)(456) 2	(14)(26)(35)(78)* 3	(123)(465) 2	(132) 4	(142635)(78)* 6	(14)(25)(36)(78) 3	(142536)(78) 6	(23)(56)* 9		
Equiv. rot.:	R^0	R^0	R_a^{π}	R^0	R^0	R_a^{π}	R_b^{π}	R_b^{π}	R_c^{π}		
A_1 :	1	1	1	1	1	1	1	1	1	:	$T_b, \alpha_{aa}, \alpha_{bb}, \alpha_{cc}$
A_2 :	1	1	1	1	1	1	−1	−1	−1	:	$T_c, \hat{J}_a, \alpha_{bc}$
A_3 :	1	1	−1	1	1	−1	1	1	−1	:	$\hat{J}_b, \alpha_{ac}, \Gamma^*$
A_4 :	1	1	−1	1	1	−1	−1	−1	1	:	$T_a, \hat{J}_c, \alpha_{ab}$
E_1 :	2	2	2	−1	−1	−1	0	0	0		
E_2 :	2	2	−2	−1	−1	1	0	0	0		
E_3 :	2	−1	0	2	−1	0	2	−1	0		
E_4 :	2	−1	0	2	−1	0	−2	1	0		
G :	4	−2	0	−2	1	0	0	0	0		

Table A-29

The group G_{48}
Example: CNPI group of CH_4

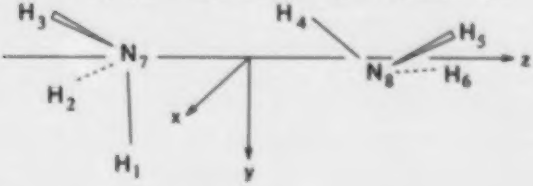


G_{48} :	E	(123)	(14)(23)	(1423)*	(23)*	E^*	(123)*	(14)(23)*	(1423)	(23)	
	1	8	3	6	6	1	8	3	6	6	
A_1^+ :	1	1	1	1	1	1	1	1	1	1	
A_2^+ :	1	1	1	−1	−1	1	1	1	−1	−1	
E^+ :	2	−1	2	0	0	2	−1	2	0	0	
F_1^+ :	3	0	−1	1	−1	3	0	−1	1	−1	
F_2^+ :	3	0	−1	−1	1	3	0	−1	−1	1	
A_1^- :	1	1	1	1	1	−1	−1	−1	−1	−1	
A_2^- :	1	1	1	−1	−1	−1	−1	−1	1	1	: Γ^*
E^- :	2	−1	2	0	0	−2	1	−2	0	0	
F_1^- :	3	0	−1	1	−1	−3	0	1	−1	1	
F_2^- :	3	0	−1	−1	1	−3	0	1	1	−1	

Table A-30

The group G_{144}

Example: Ammonia dimer (with moiety inversion)



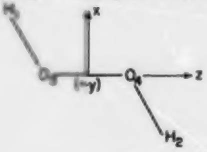
G_{144}:	E	(12)	(12)(45)	(123)	(14)(25)(36)(78)	(12)(456)	(123)(456)	(14)(2536)(78)	(142536)(78)	E^*	(12)*	(12)(45)*	(123)*	(14)(25)(36)(78)*	(12)(456)*	(123)(456)*	(14)(2536)(78)*	(142536)(78)*	
	1	6	9	4	6	12	4	18	12	1	6	9	4	6	12	4	18	12	
A_1^+ :	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
A_2^+ :	1	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	−1	−1	1	1	−1	
B_1^+ :	1	1	1	1	−1	1	1	−1	−1	1	1	1	1	−1	1	1	−1	−1	
B_2^+ :	1	−1	1	1	1	−1	1	−1	1	1	−1	1	1	1	−1	1	−1	1	
E^+ :	2	0	−2	2	0	0	2	0	0	2	0	−2	2	0	0	2	0	0	
G_1^+ :	4	2	0	1	0	−1	−2	0	0	4	2	0	1	0	−1	−2	0	0	
G_2^+ :	4	−2	0	1	0	1	−2	0	0	4	−2	0	1	0	1	−2	0	0	
G_3^+ :	4	0	0	−2	−2	0	1	0	1	4	0	0	−2	−2	0	1	0	1	
G_4^+ :	4	0	0	−2	2	0	1	0	−1	4	0	0	−2	2	0	1	0	−1	
A_1^- :	1	1	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1	−1	: Γ^*
A_2^- :	1	−1	1	1	−1	−1	1	1	−1	−1	1	−1	−1	1	1	−1	−1	1	
B_1^- :	1	1	1	1	−1	1	1	−1	−1	−1	−1	−1	−1	1	−1	−1	1	1	
B_2^- :	1	−1	1	1	1	−1	1	−1	1	−1	1	−1	−1	−1	1	−1	1	−1	
E^- :	2	0	−2	2	0	0	2	0	0	−2	0	2	−2	0	0	−2	0	0	
G_1^- :	4	2	0	1	0	−1	−2	0	0	−4	−2	0	−1	0	1	2	0	0	
G_2^- :	4	−2	0	1	0	1	−2	0	0	−4	2	0	−1	0	−1	2	0	0	
G_3^- :	4	0	0	−2	−2	0	1	0	1	−4	0	0	2	2	0	−1	0	−1	
G_4^- :	4	0	0	−2	2	0	1	0	−1	−4	0	0	2	−2	0	−1	0	1	

The labeling of the irreducible representations is as given by Odutola, Dyke, Howard, and Muenter (1979).

Table A-31

The group G_4(EM)

Example: Hydrogen peroxide (with torsional tunneling)[a,b]



G_4(EM):	E 1	a 1	b 1	ab 1	E' 1	$E'a$ 1	$E'b$ 1	$E'ab$ 1		
Equiv. rot.:	R^0	$R^{\pi}_{\pi/2}$	R_x^{π}	R_z^{π}	R_z^{π}	R_x^{π}	$R^{\pi}_{3\pi/2}$	R^0		
A_{gs}:	1	1	1	1	1	1	1	1	:	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
A_{us}:	1	1	−1	−1	1	1	−1	−1	:	$\hat{J}_{\rho}, \Gamma^*$
B_{gs}:	1	−1	−1	1	1	−1	−1	1	:	$\hat{J}_z, \alpha_{xy}$
B_{us}:	1	−1	1	−1	1	−1	1	−1	:	T_z
A_{gd}:	1	1	−1	−1	−1	−1	1	1	:	$\hat{J}_y, \alpha_{xz}$
A_{ud}:	1	1	1	1	−1	−1	−1	−1	:	T_y
B_{gd}:	1	−1	1	−1	−1	1	−1	1	:	$\hat{J}_x, \alpha_{yz}$
B_{ud}:	1	−1	−1	1	−1	1	1	−1	:	T_x

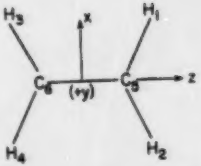
[a] For space fixed coordinates $a = (12)(34)$, $b = E^*$ and $E' = E$. See page 525.

[b] For the definitions of the Euler angle transformations see Table 15-11.

Table A-32

The group G_{16}(EM)

Example: Ethylene (with torsional tunneling)[a,b]

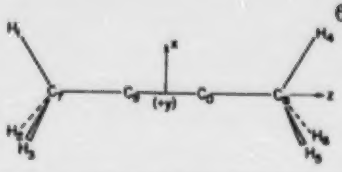


G_{16}(EM):	E 1	a 4	a^2 1	b 2	ab 4	c 2	ac 4	a^2c 2	bc 2	abc 4	E' 1	a^2E' 1	bE' 2	bcE' 2	
Equiv. rot.:	R^0	$R_z^{\pi/2}$	R_z^{π}	R_{π}^{π}	$R^{\pi}_{3\pi/4}$	R_{π}^{π}	$R^{\pi}_{3\pi/4}$	$R^{\pi}_{\pi/2}$	R^0	$R_z^{5\pi/2}$	R_z^{π}	$R^{2\pi}$	$R^{\pi}_{3\pi/2}$	R_z^{π}	
A_{1g}^+ :	1	1	1	1	1	1	1	1	1	1	1	1	1	1	: $\alpha_{zz}, (\alpha_{xx}+\alpha_{yy})$
A_{2u}^+ :	1	1	1	−1	−1	1	1	1	−1	−1	1	1	−1	−1	
B_{1g}^+ :	1	−1	1	1	−1	1	−1	1	1	−1	1	1	1	1	: $(\alpha_{xx}-\alpha_{yy})$
B_{2u}^+ :	1	−1	1	−1	1	1	−1	1	−1	1	1	1	−1	−1	: T_z
E^+ :	2	0	−2	0	0	2	0	−2	0	0	2	−2	0	0	
A_{1u}^- :	1	1	1	1	1	−1	−1	−1	−1	−1	1	1	1	−1	
A_{2g}^- :	1	1	1	−1	−1	−1	−1	−1	1	1	1	1	−1	1	: $\hat{J}_z$
B_{1u}^- :	1	−1	1	1	−1	−1	1	−1	−1	1	1	1	1	−1	: $\Gamma^*, \hat{J}_\rho$
B_{2g}^- :	1	−1	1	−1	1	−1	1	−1	1	−1	1	1	−1	1	: α_{xy}
E^- :	2	0	−2	0	0	−2	0	2	0	0	2	−2	0	0	
E_1 :	2	0	2	2	0	0	0	0	0	0	−2	−2	−2	0	
E_2 :	2	0	2	−2	0	0	0	0	0	0	−2	−2	2	0	
E_g :	2	0	−2	0	0	0	0	0	2	0	−2	2	0	−2	: $(\hat{J}_x, \hat{J}_y), (\alpha_{xz}, \alpha_{yz})$
E_u :	2	0	−2	0	0	0	0	0	−2	0	−2	2	0	2	: (T_x, T_y)

[a] For space fixed coordinates $a = (1423)(56)^*, b = (13)(24)(56), c = E^*$, and $E' = E$. See page 531.

[b] For the definitions of the Euler angle transformations see Table 15-16.

Table A-33
The group $G_{36}(EM)$
Example: Dimethylacetylene (with torsional tunneling)[a,b]



$G_{36}(EM)$:	E	ab	c	ab^5	a^4	b^2c	cd	b^4cd	d
	1	2	3	2	4	6	3	6	9
Equiv. rot.:	R^0	R^0	R_z^π	$R_z^{2\pi/3}$	$R_z^{4\pi/3}$	$R_z^{\pi/3}$	R_0^π	$R^\pi_{2\pi/3}$	$R^\pi_{\pi/2}$
A_{1s} :	1	1	1	1	1	1	1	1	1
A_{2s} :	1	1	1	1	1	1	−1	−1	−1
A_{3s} :	1	1	−1	1	1	−1	1	1	−1
A_{4s} :	1	1	−1	1	1	−1	−1	−1	1
E_{1s} :	2	2	2	−1	−1	−1	0	0	0
E_{2s} :	2	2	−2	−1	−1	1	0	0	0
E_{3s} :	2	−1	0	2	−1	0	2	−1	0
E_{4s} :	2	−1	0	2	−1	0	−2	1	0
G_s :	4	−2	0	−2	1	0	0	0	0
A_{1d} :	1	1	1	1	1	1	1	1	1
A_{2d} :	1	1	1	1	1	1	−1	−1	−1
A_{3d} :	1	1	−1	1	1	−1	1	1	−1
A_{4d} :	1	1	−1	1	1	−1	−1	−1	1
E_{1d} :	2	2	2	−1	−1	−1	0	0	0
E_{2d} :	2	2	−2	−1	−1	1	0	0	0
E_{3d} :	2	−1	0	2	−1	0	2	−1	0
E_{4d} :	2	−1	0	2	−1	0	−2	1	0
G_d :	4	−2	0	−2	1	0	0	0	0

E'	$E'ab$	$E'c$	$E'ab^5$	$E'a^4$	$E'b^2c$	$E'cd$	$E'b^4cd$	$E'd$		
1	2	3	2	4	6	3	6	9		
R_z^π	R_z^π	R^0	$R_z^{5\pi/3}$	$R_z^{\pi/3}$	$R_z^{4\pi/3}$	$R^\pi_{\pi/2}$	$R^\pi_{\pi/6}$	R_0^π		
1	1	1	1	1	1	1	1	1	:	$(\alpha_{xx}+\alpha_{yy}), \alpha_{zz}$
1	1	1	1	1	1	−1	−1	−1	:	J_z
1	1	−1	1	1	−1	1	1	−1	:	J_ρ, Γ^*
1	1	−1	1	1	−1	−1	−1	1	:	T_z
2	2	2	−1	−1	−1	0	0	0	:	$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$
2	2	−2	−1	−1	1	0	0	0		
2	−1	0	2	−1	0	2	−1	0		
2	−1	0	2	−1	0	−2	1	0		
4	−2	0	−2	1	0	0	0	0		
−1	−1	−1	−1	−1	−1	−1	−1	−1		
−1	−1	−1	−1	−1	−1	1	1	1		
−1	−1	1	−1	−1	1	−1	−1	1		
−1	−1	1	−1	−1	1	1	1	−1		
−2	−2	−2	1	1	1	0	0	0	:	(T_x, T_y)
−2	−2	2	1	1	−1	0	0	0	:	$(J_x, J_y), (\alpha_{xz}, \alpha_{yz})$
−2	1	0	−2	1	0	−2	1	0		
−2	1	0	−2	1	0	2	−1	0		
−4	2	0	2	−1	0	0	0	0		

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[a] For space fixed coordinates $a = (123), b = (456), c = (14)(26)(35)(78)(90)^*, d = (23)(56)^*$, and $E' = E$. See page 520.

[b] For the definitions of the Euler angle transformations see Table 15-8.

APPENDIX *B*

The Correlation Tables

In this Appendix there are four types of correlation table.

In Table B-1 the representations $D^{(0)}$ through $D^{(3)}$ of the spin double group of the three-dimensional molecular rotational group $\boldsymbol{K}(\mathrm{mol})^2$ are reduced onto the molecular rotation groups $\boldsymbol{D}_{\infty}{}^2$ and $\boldsymbol{D}_2{}^2$. The rotational states of a spherical top molecule can be labeled $D^{(J)}$ in $\boldsymbol{K}(\mathrm{mol})^2$ according to the value of J. The rotational states of a symmetric top molecule can be labeled Σ^+ (or Σ^-), $\Pi, \Delta, \ldots$, in $\boldsymbol{D}_{\infty}{}^2$ as $K = 0$ with J even (or $K = 0$ with J odd), $K = 1$, $K = 2$, $\ldots$, respectively, and the rotational states of an asymmetric top molecule can be labeled A, B_a, B_b, and B_c in $\boldsymbol{D}_2{}^2$ as K_aK_c is ee, eo, oo, and oe (o = odd and e = even). Tables 12-15 and 12-16 were used in these reductions.

In Table B-2 the representations $D^{(0)}$ through $D^{(3)}$ of $\boldsymbol{K}(\mathrm{mol})^2$ are reduced onto the representations of groups given in Appendices 18-1 and **A** by using the equivalent rotations of the elements of the group. We first reduce $\boldsymbol{K}(\mathrm{mol})$ onto the equivalent rotation group of the MS (or EMS) group, and then make use of the isomorphism or homomorphism of the MS (or EMS) group onto the equivalent rotation group in order to obtain the final result. The equivalent rotation group is the group of all distinct equivalent rotations of the MS (or EMS) group concerned; e.g., for the C_{3v}(M) group it is $\boldsymbol{D}_3 = \{E, R_z^{2\pi/3}, R_z^{4\pi/3}, R_{\pi/6}^{\pi}, R_{\pi/2}^{\pi}, R_{5\pi/6}^{\pi}\}$. From this table the symmetry Γ_{rot} of the rotational states with $J \leq 3$ of each molecule in its MS (or EMS) group can be obtained. The species of Hund's case (a) electron spin functions in these groups can be obtained from this table by identifying the representations of $\boldsymbol{K}(\mathrm{mol})^2$ with $D^{(S)}$.

In Table B-3 the correlations of the representations of the molecular point groups of bent and linear molecules are given for use in determining the correlation of the symmetry of the electronic states of a linear triatomic molecule with those obtained by bending the molecule.

In Table B-4 reverse correlation tables, with statistical weights, are given for some common nonrigid molecules. For a rigid methanol molecule the C_s(M) group is $\{E, (23)^*\}$ if we take the rigid conformer as having O–C–H$_1$ coplanar with the C–O–H group. For a rigid methyl silane molecule the C_{3v}(M) group of a conformer is $\{E, (123)(465), (132)(456), (12)(46)^*, (13)(45)^*, (23)(56)^*\}$ regardless of whether it is eclipsed or staggered. For a rigid acetone molecule in the conformation indicated in Table A-28 the C_{2v}(M) group is $\{E, (14)(25)(36)(78), (23)(56)^*, (14)(26)(35)(78)^*\}$. The results in Table B-4 are of use when the tunneling splitting are small, and the statistical weights should help in the assignments of the states.

Table B-1

The correlation table of $\boldsymbol{K}(\mathrm{mol})^2$ with the molecular rotational groups $\boldsymbol{D}_{\infty}{}^2$ and $\boldsymbol{D}_2{}^2$

$\boldsymbol{K}(\mathrm{mol})^2$	$\boldsymbol{D}_{\infty}{}^2$	$\boldsymbol{D}_2{}^2$
$D^{(0)}$	Σ^+	A
$D^{(1/2)}$	$E_{1/2}$	$E_{1/2}$
$D^{(1)}$	$\Sigma^- \oplus \Pi$	$B_a \oplus B_b \oplus B_c$
$D^{(3/2)}$	$E_{1/2} \oplus E_{3/2}$	$2E_{1/2}$
$D^{(2)}$	$\Sigma^+ \oplus \Pi \oplus \Delta$	$2A \oplus B_a \oplus B_b \oplus B_c$
$D^{(5/2)}$	$E_{1/2} \oplus E_{3/2} \oplus E_{5/2}$	$3E_{1/2}$
$D^{(3)}$	$\Sigma^- \oplus \Pi \oplus \Delta \oplus \Phi$	$A \oplus 2B_a \oplus 2B_b \oplus 2B_c$

Table B-2

The correlation of $\boldsymbol{K}(\mathrm{mol})^2$ with the spin double groups of MS and EMS groups

(i) Asymmetric top molecules

$\boldsymbol{K}(\mathrm{mol})^2$	$C_s(\mathrm{M})^2$	$C_i(\mathrm{M})^2$	$C_2(\mathrm{M})^2$	$C_{2v}(\mathrm{M})^2$	$C_{2h}(\mathrm{M})^2$	$D_{2h}(\mathrm{M})^2$
$D^{(0)}$	A'	A_g	A	A_1	A_g	A_g
$D^{(1/2)}$	$E_{1/2}$	$E_{g/2}$	$E_{1/2}$	$E_{1/2}$	$E_{g/2}$	$E_{g/2}$
$D^{(1)}$	$A' \oplus 2A''$	$3A_g$	$A \oplus 2B$	$A_2 \oplus B_1 \oplus B_2$	$A_g \oplus 2B_g$	$B_{1g} \oplus B_{2g} \oplus B_{3g}$
$D^{(3/2)}$	$2E_{1/2}$	$2E_{g/2}$	$2E_{1/2}$	$2E_{1/2}$	$2E_{g/2}$	$2E_{g/2}$
$D^{(2)}$	$3A' \oplus 2A''$	$5A_g$	$3A \oplus 2B$	$2A_1 \oplus A_2 \oplus B_1 \oplus B_2$	$3A_g \oplus 2B_g$	$2A_g \oplus B_{1g} \oplus B_{2g} \oplus B_{3g}$
$D^{(5/2)}$	$3E_{1/2}$	$3E_{g/2}$	$3E_{1/2}$	$3E_{1/2}$	$3E_{g/2}$	$3E_{g/2}$
$D^{(3)}$	$3A' \oplus 4A''$	$7A_g$	$3A \oplus 4B$	$A_1 \oplus 2A_2 \oplus 2B_1 \oplus 2B_2$	$3A_g \oplus 4B_g$	$A_g \oplus 2B_{1g} \oplus 2B_{2g} \oplus 2B_{3g}$

Table B-2 continued

(ii) Symmetric top, spherical top, and linear molecules

$K(\mathrm{mol})^2$	$D_{2d}(\mathrm{M})^2$	$C_{3v}(\mathrm{M})^2$	$D_{3h}(\mathrm{M})^2$	$D_{3d}(\mathrm{M})^2$
$D^{(0)}$	A_1	A_1	A_1'	A_{1g}
$D^{(1/2)}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{g/2}$
$D^{(1)}$	$A_2 \oplus E$	$A_2 \oplus E$	$A_2' \oplus E''$	$A_{2g} \oplus E_g$
$D^{(3/2)}$	$E_{1/2} \oplus E_{3/2}$	$E_{1/2} \oplus E_{3/2}$	$E_{1/2} \oplus E_{3/2}$	$E_{g/2} \oplus E_{3g/2}$
$D^{(2)}$	$A_1 \oplus B_1 \oplus B_2 \oplus E$	$A_1 \oplus 2E$	$A_1' \oplus E' \oplus E''$	$A_{1g} \oplus 2E_g$
$D^{(5/2)}$	$E_{1/2} \oplus 2E_{3/2}$	$2E_{1/2} \oplus E_{3/2}$	$E_{1/2} \oplus E_{3/2} \oplus E_{5/2}$	$2E_{g/2} \oplus E_{3g/2}$
$D^{(3)}$	$A_2 \oplus B_1 \oplus B_2 \oplus 2E$	$A_1 \oplus 2A_2 \oplus 2E$	$A_1'' \oplus A_2' \oplus A_2''$ $\oplus E' \oplus E''$	$A_{1g} \oplus 2A_{2g} \oplus 2E_g$

$K(\mathrm{mol})^2$	$T_d(\mathrm{M})^2$	$O_h(\mathrm{M})^2$	$I_h(\mathrm{M})^2$
$D^{(0)}$	A_1	A_{1g}	A_g
$D^{(1/2)}$	$E_{1/2}$	$E_{1g/2}$	$E_{1g/2}$
$D^{(1)}$	F_1	F_{1g}	F_{1g}
$D^{(3/2)}$	$G_{3/2}$	$G_{3g/2}$	$G_{3g/2}$
$D^{(2)}$	$E \oplus F_2$	$E_g \oplus F_{2g}$	H_g
$D^{(5/2)}$	$G_{3/2} \oplus E_{5/2}$	$G_{3g/2} \oplus E_{5g/2}$	$I_{5g/2}$
$D^{(3)}$	$A_2 \oplus F_1 \oplus F_2$	$A_{2g} \oplus F_{1g} \oplus F_{2g}$	$F_{2g} \oplus G_g$

$K(\mathrm{mol})^2$	$C_{\infty v}(\mathrm{EM})^2$	$D_{\infty h}(\mathrm{EM})^2$
$D^{(0)}$	Σ^+	Σ_g^+
$D^{(1/2)}$	$E_{1/2}$	$E_{g/2}$
$D^{(1)}$	$\Sigma^- \oplus \Pi$	$\Sigma_g^- \oplus \Pi_g$
$D^{(3/2)}$	$E_{1/2} \oplus E_{3/2}$	$E_{g/2} \oplus E_{3g/2}$
$D^{(2)}$	$\Sigma^+ \oplus \Pi \oplus \Delta$	$\Sigma_g^+ \oplus \Pi_g \oplus \Delta_g$
$D^{(5/2)}$	$E_{1/2} \oplus E_{3/2} \oplus E_{5/2}$	$E_{g/2} \oplus E_{3g/2} \oplus E_{5g/2}$
$D^{(3)}$	$\Sigma^- \oplus \Pi \oplus \Delta \oplus \Phi$	$\Sigma_g^- \oplus \Pi_g \oplus \Delta_g \oplus \Phi_g$

Table B-2 continued
(iii) Nonrigid molecules

$\boldsymbol{K}(\mathrm{mol})^2$	$G_6{}^2$	G_{12}^2	G_{18}^2	G_{36}^2
$D^{(0)}$	A_1	$A_1{}'$	A_1	A_1
$D^{(1/2)}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$
$D^{(1)}$	$A_1 \oplus 2A_2$	$A_2{}' \oplus A_1'' \oplus A_2''$	$A_2 \oplus E_1$	$A_2 \oplus A_3 \oplus A_4$
$D^{(3/2)}$	$2E_{1/2}$	$2E_{1/2}$	$E_{1/2} \oplus E_{3/2}$	$2E_{1/2}$
$D^{(2)}$	$3A_1 \oplus 2A_2$	$2A_1{}' \oplus A_2{}' \oplus A_1'' \oplus A_2''$	$A_1 \oplus 2E_1$	$2A_1 \oplus A_2 \oplus A_3 \oplus A_4$
$D^{(5/2)}$	$3E_{1/2}$	$3E_{1/2}$	$2E_{1/2} \oplus E_{3/2}$	$3E_{1/2}$
$D^{(3)}$	$3A_1 \oplus 4A_2$	$A_1{}' \oplus 2A_2{}' \oplus 2A_1'' \oplus 2A_2''$	$A_1 \oplus 2A_2 \oplus 2E_1$	$A_1 \oplus 2A_2 \oplus 2A_3 \oplus 2A_4$

$\boldsymbol{K}(\mathrm{mol})^2$	$G_4(\mathrm{EM})^2$	$G_{16}(\mathrm{EM})^2$	$G_{36}(\mathrm{EM})^2$
$D^{(0)}$	A_1	$A_1{}^+$	A_1
$D^{(1/2)}$	$E_{g/2}$	$E_{g/2}$	$E_{1/2}$
$D^{(1)}$	$B_1 \oplus A_{2d} \oplus B_{2d}$	$A_2{}^- \oplus E_{3d}$	$A_2 \oplus E_{2d}$
$D^{(3/2)}$	$2E_{g/2}$	$E_{g/2} \oplus E_{3g/2}$	$E_{1/2} \oplus E_{3/2}$
$D^{(2)}$	$2A_1 \oplus B_1 \oplus A_{2d} \oplus B_{2d}$	$A_1{}^+ \oplus B_1{}^+ \oplus B_2{}^- \oplus E_{3d}$	$A_1 \oplus E_1 \oplus E_{2d}$
$D^{(5/2)}$	$3E_{g/2}$	$E_{g/2} \oplus 2E_{3g/2}$	$E_{1/2} \oplus E_{3/2} \oplus E_{5/2}$
$D^{(3)}$	$A_1 \oplus 2B_1 \oplus 2A_{2d} \oplus 2B_{2d}$	$A_2{}^- \oplus B_1{}^+ \oplus B_2{}^- \oplus 2E_{3d}$	$A_2 \oplus A_{3d} \oplus A_{4d}$ $\oplus E_1 \oplus E_{2d}$

Table B-3

Correlation of species of electronic states of a linear triatomic molecule[a] with species of electronic states obtained when molecule is bent[a]

$D_{\infty h}$	C_{2v}	$C_{\infty v}$	C_s
Σ_g^+	A_1	Σ^+	A'
Σ_u^+	B_2	Σ^-	A''
Σ_g^-	B_1	Π	$A' \oplus A''$
Σ_u^-	A_2	Δ	$A' \oplus A''$
Π_g	$A_2 \oplus B_2$	⋮	⋮
Π_u	$A_1 \oplus B_1$		
Δ_g	$A_1 \oplus B_1$		
Δ_u	$A_2 \oplus B_2$		
⋮	⋮		

[a] In $D_{\infty h}$ or $C_{\infty v}$.

[b] In C_{2v} or C_s.

Table B-4

Reverse correlation Tables for nonrigid molecules with statistical weights (C = ^{12}C, N = ^{14}N, and O = ^{16}O)

(i) NH_3[a]

C_{3v}(M)	D_{3h}(M)
$A_1(12)$	$A_1'(0) \oplus A_2''(12)$
$A_2(12)$	$A_2'(12) \oplus A_1''(0)$
$E(12)$	$E'(6) \oplus E''(6)$

(ii) CH_3OH[b]

C_s(M)	G_6
$A'(8)$	$A_1(4) \oplus E(4)$
$A''(8)$	$A_2(4) \oplus E(4)$

Table B-4 continued

(iii) SiH_3CH_3[c]

$C_{3v}(M)$	G_{18}
$A_1(24)$	$A_1(16) \oplus E_4(8)$
$A_2(24)$	$A_2(16) \oplus E_4(8)$
$E(40)$	$E_1(16) \oplus E_2(16) \oplus E_3(8)$

(iv) CH_3COCH_3[d]

$C_{2v}(M)$	G_{36}
$A_1(28)$	$A_1(6) \oplus E_1(4) \oplus E_3(2) \oplus G(16)$
$A_2(28)$	$A_3(6) \oplus E_2(4) \oplus E_3(2) \oplus G(16)$
$B_1(36)$	$A_2(10) \oplus E_1(4) \oplus E_4(6) \oplus G(16)$
$B_2(36)$	$A_4(10) \oplus E_2(4) \oplus E_4(6) \oplus G(16)$

(v) H_2O_2[e]

$C_2(M)$	G_4	G_8
$A(2)$	$A_1(1) \oplus A_2(1)$	$A_1{}'(1) \oplus A_1''(0) \oplus A_2{}'(1) \oplus A_2''(0)$
$B(6)$	$B_1(3) \oplus B_2(3)$	$B_1{}'(0) \oplus B_1''(3) \oplus B_2{}'(0) \oplus B_2''(3)$

(vi) C_2H_4[f]

$D_{2h}(M)$	G_{16}
$A_g(7)$	$A_1{}^+(1) \oplus B_1{}^+(6)$
$A_u(7)$	$A_1{}^-(6) \oplus B_1{}^-(1)$
$B_{1g}(3)$	$A_2{}^-(0) \oplus B_2{}^-(3)$
$B_{1u}(3)$	$A_2{}^+(3) \oplus B_2{}^+(0)$
$B_{2g}(3)$	$E^-(3)$
$B_{2u}(3)$	$E^+(3)$
$B_{3g}(3)$	$E^+(3)$
$B_{3u}(3)$	$E^-(3)$

(vii) C_2H_6[g]

$D_{3d}(M)$	G_{36}
$A_{1g}(8)$	$A_1(6) \oplus E_3(2)$
$A_{1u}(8)$	$A_3(6) \oplus E_3(2)$
$A_{2g}(16)$	$A_2(10) \oplus E_4(6)$
$A_{2u}(16)$	$A_4(10) \oplus E_4(6)$
$E_g(20)$	$E_1(4) \oplus G(16)$
$E_u(20)$	$E_2(4) \oplus G(16)$

(viii) CH_4[h]

$T_d(M)$	G_{48}
$A_1(5)$	$A_1{}^+(0) \oplus A_1{}^-(5)$
$A_2(5)$	$A_2{}^+(5) \oplus A_2{}^-(0)$
$E(2)$	$E^+(1) \oplus E^-(1)$
$F_1(3)$	$F_1{}^+(3) \oplus F_1{}^-(0)$
$F_2(3)$	$F_2{}^+(0) \oplus F_2{}^-(3)$

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[a] See Tables A-6 and A-10.

[b] See Tables A-2 and A-22.

[c] See Tables A-6 and A-26.

[d] See Tables A-5 and A-28.

[e] See Tables A-4, A-21, and A-23.

[f] See Tables A-9, A-23, and 8-2.

[g] See Tables A-13 and A-33.

[h] See Tables A-14 and A-29.

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